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(54) Chain extended urethane diacrylate and dental impression formation.

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Description

Background of the Invention

This invention relates to a composition of matter that is a urethane diacrylate which is especially useful as a compound for use in compositions for forming impressions of mammalian tissue especially in dental applications - compositions that accurately conform to dental surfaces to be recorded, and to a method of producing the urethane diacrylate. The invention also relates to such impression materials that are free radical polymerizable resins and contain alkyl benzensulfonyl titanate, polymerization initiator and filler.

Methods of forming dental impressions are well known, as are dental impression materials that are capable of accurately reproducing the surface contours and dimensions of oral tissues required in preparing dental prostheses. Since anatomic structures and preparations for prosthetic appliances are usually undercut, preferred impression materials are elastic or rubbery, ranging from gels, such as agar or algin preparations, to elastomers, such as rubbers, silicones, and polyethers. The nonaqueous elastomers are preferred because of their extreme dimensional accuracy and their relative stability under ambient conditions. In spite of all the improvements which have characterized current dental impression materials, they are still greatly limited by clinical factors when they are used in vivo.

It is known to prepare elastomeric impression materials by taking two separate pastes (one containing catalyst and the other containing an accelerator), placing measured amounts of each on a pad of parchment or polyethylene-coated paper and immediately mixing them with a spatula into a substantially homogeneous mass. Such impression materials must be used immediately after mixing; and while curing to set is rapid, it must be timed to allow placement by fast and slow dental practitioners and because the curing time is built in, special problems cannot be controlled with any degree of accuracy by the dental practitioner. Also, the act of mixing tends to introduce air bubbles into the viscous pastes and these bubbles are difficult to eliminate, tending to cause surface imperfections in the finished impression or distortion of the impression. Mixing is inconvenient and a source of inconsistency.

In the usual practice, a dental practitioner places the mixed paste in juxtaposition to the dental tissues, using either a supporting tray to contain the paste or a combination of a placement syringe and a supporting tray. The dental practitioner or dentist and the patient then wait, sometimes for ten minutes, for the polymerization reaction to progress to completion and the material to become sufficiently elastic so that the impression may be removed from the tissue without distortion of the remembered shape or form. The rate of faulty impressions is quite high due to the patient's natural tendency to move during this time and a gagging reflex is common. The dental practitioner loses valuable time while he is thus inactivated, plus time needed for the often required retakes.

Materials commonly used for taking impressions are polysiloxanes such as described in United States Patent Number 3,950,300, polyethers such as described in United States Patent Number 3,453,242, and other elastomeric materials having properties more fully described in American Dental Association Specification 19.

EP-A-0 173 085 describes a urethane polyacrylate having at least one isocyanato acrylic pendent group.

Summary of the Invention

The new urethane polyacrylate having at least one isocyanato acrylic pendent group provides an excellent dental composition component that, in preferred forms, is non-toxic in use in the oral cavity and will assume a permanent elastomeric memory when cured. When the urethane polyacrylate is provided with an initiator activated by actinic light within the visible light range of 360 to 600 nanometers it can be substantially stable against assuming a permanent remembered form when stored actinic light free, and then on exposure to light filtered to limited wavelengths within the visible light range for one (1) minute cure to a depth of 2,54 cm (one (1) inch).

The preferred compound is a chain extended urethane polyacrylate made according to the following preferred method. First, a polyhydroxy compound is reacted with a polyisocyanate forming a first reaction product having about 2 equivalents of reactive isocyanate. This first reaction product is then reacted with less than two equivalents of a compound having an acrylic pendent radical and another reactive site preferentially reacting with the first reaction product, forming a second reaction product. The second reaction product is then reacted with a polyhydroxy compound to form a third reaction product. This third reaction product is then reacted with an isocyanato acrylate compound to form the urethane polyacrylate.

According to the present invention a new impression material for application to mammalian tissue and curing in contact therewith to set the impression is provided. The impression material includes a free radical polymerizable resin, alkyl benzensulfonyl titanate, polymerization initiator and filler. Also provided is a method for using the new impression material.

Description of the Preferred Embodiment

The present invention provides an elastomeric dental impression material composition for use in dentistry as defined in Claim 1. A composition for use as a soft denture liner makes use of a compound having the following general formula:

$R_1\{A\}R_2$

wherein

$$R_1 \text{ is } CH_2 = \overset{R_3}{\underset{|}{C}} - \overset{O}{\overset{\|}{C}} - O\{R_4\}O - \overset{O}{\overset{\|}{C}} - \overset{H}{\underset{|}{N}} -$$

and

R_2 is as defined in Claim 1 and each independently preferably have from 5 to 100 C, more preferably 5 to 15 C and most preferably 6 to 11 C.

R_3 is H, alkyl, sub alkyl, aryl, sub aryl, F, CN. (The term sub as used in this application means substituted, which means that at least one non C or H atom would be present or a radical such as a benzene ring would be present. By acrylic it is meant any pendent acrylic radical, by diacrylic it is meant a radical or a compound with two pendent acrylic radicals.)

R_3 may be the same or different in each position.

R_3 is preferably methyl.

R_4 is a divalent hydrocarbon radical or divalent sub hydrocarbon radical and may be straight or branched chain or cyclic or a combination thereof. By cyclic it is meant to include aromatic and heterocyclic compounds.

R_4 preferably has from 2 to 100 C, more preferably R_4 is an aliphatic radical having from 2 to 100 C, more preferably 2 to 10 C and most preferably 2 to 6 C.

[A] is any polyurethane, polyester or polyether oligomer. (By poly as used in this application it is meant two or more. By oligomer it is meant a molecular weight of between 500 and 5000. The moleculer weight of the oligomer and its resulting physical characteristics can be controlled by carefully choosing the substitutents used to make up the oligomer in a manner that is well known to those skilled in the art. For example, [A] may be chosen to be a low molecular weight polyether when a relatively rigid polymer is desired, and [A] and other sutstituents may be chosen to have a high molecular weight when a relatively soft pliable polymer is desired. As will be recognized by those skilled in the art, the concentration and the type of fillers used in the polymer, and other factors will affect the properties of the polymer to some extent. In general, however, when a relatively rigid polymer is desired the molecular weight of the oligomer should be in the range of 500-2000 and preferably 650-1500. When a soft, pliable polymer is desired, the oligomer will have a molecular weight in the range of 1500-5000, preferably 2000-4000.

The soft, pliable resins have elastic properties and may be characterized generally at being capable of about 50% or more elongation from the unstressed state before rupture or tearing after being cured.

The rigid polymers may be characterized generally as being capable of about 50% or less elongation from its unstressed state, before tearing or rupture.

The elongation property described herein is a characteristic of the unfilled resin.

The term backbone as used in this application means the structure of the oligomer between the two urethane groups closest to the terminal ends of the molecule).

A presently preferred composition, which is an important aspect of the present invention, is where A is represented by $[R_5]$-X-$[R_6]$.

X is a polyurethane and R_5-X and R_6-X are joined by a urethane or polyurethane linkage.

X may broadly contain any hydrocarbon or sub hydrocarbon radical and may be straight or branched chain or cyclic or a combination thereof and may also be one or more of the following radicals: siloxane, sub siloxane, sulfone, etc., but is preferably a polyether or a polyester or a mixture thereof, most preferably X is a polyether and the polyether radical is a straight chain.

R_5 and R_6 are each independently divalent hydrocarbon radicals or divalent subs hydrocarbon radicals and may be straight or branched chain or cyclic or a combination thereof and may also be siloxane or subs siloxane radicals.

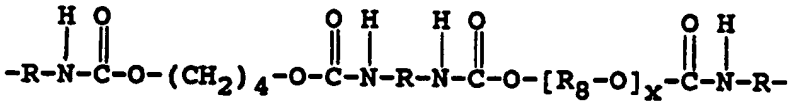
By lower alkyl, it is meant alkyl or substituted (sub) alkyl of 1-25 carbons, preferably 1-15 carbons and more preferably 1-12 carbons. By alkylene is meant an alkyl group having 2 to 40 carbon atoms, preferably 2 to 30 carbon atoms and most preferably 2 to 15 carbon atoms, unless otherwise specifically defined.

Sub or substituent is not limited to but is meant to include, as representative examples, radicals selected from the group consisting of halogen, lower alkyl, oxy-lower-alkyl, silyl-lower-alkyl, phenyl, halo phenyl, alkoxyphenyl, trihalomethyl, dihalomethyl, and similar substituents where lower alkyl has 1 to 6 carbons.

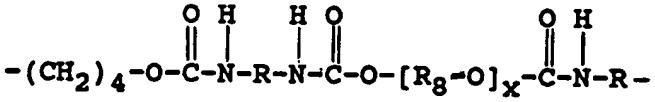
R_5 and R_6 preferably have from 3 to 100 C, more preferably R_5 and R_6 are aliphatic radicals having from 2 to 100 C, more preferably 2 to 10 C. R_5 and R_6 may be the same or different.

The person skilled in the art would tailor the [A] radical to achieve such characteristics as he may choose. The particularly preferred [A] radical, especially with both R_5 and R_6 joined to X by a urethane linkage with X being of substantial molecular weight and both R_5 and R_6 of low molecular weight, is of special preferred merit, especially in the more preferred embodiments of the present invention.

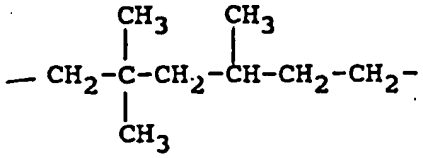
In the preferred embodiment A is the radical



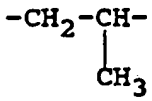
or A is



where R is alkyl having 2-25 carbon atoms and R is preferably the group



and R_8 is alkyl of 2-25 carbon atoms and preferably is the group



and x is 10 to 100

In the preferred embodiment, the polymers of the present invention can be broadly described as comprising a molar ratio of polyol/polyisocyanate/hydroxyalkyl methacrylate/dihydroxy compound/isocyanatoacrylate of

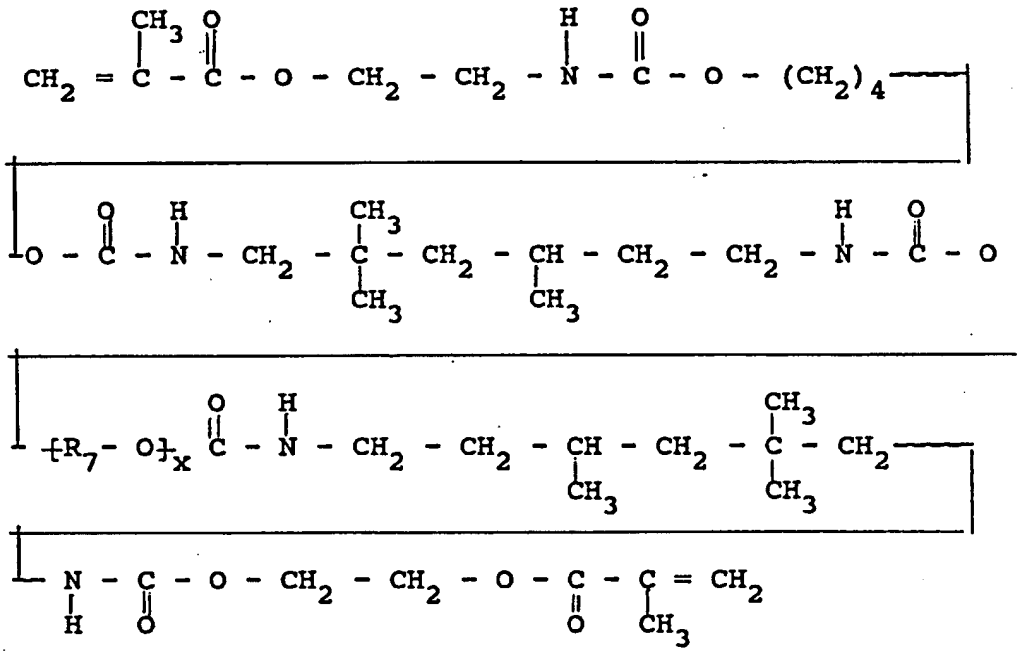
1:2:1-1.5:1-1.5:0.5-1.

In the preferred reaction:

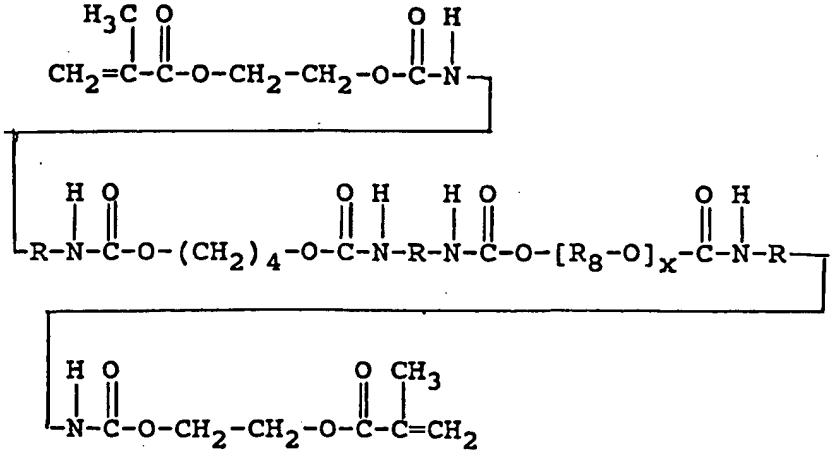
R_1 is a radical preferably formed by reacting a hydroxy acrylate with an isocyanate group on a prepolymer polyurethane oligomer and is drawn to include the urethane group contributed by the isocyanate, or a radical contributed entirely by an isocyanato acrylate when the isocyanato acrylate is reacted with a hydroxy group on a prepolymer polyurethane oligomer.

In $[R_5]$-X-$[R_6]$, R_5 would be the terminal radical in the prepolymer polyurethane oligomer when the terminal urethane group has been drawn as part of R_1. For clarity of explanation, in Example 1 this would be the trimethyl hexamethylene radical from trimethyl hexamethylene diisocyanate and would include the other urethane group contributed by the diisocyanate. R_6 would be the oxyalkylene residue of the 1,4 butane diol.

The more preferred compounds have the formula:



where R_7 is alkylene or sub alkylene and x is 10 to 100; or



wherein R is alkyl of 2 to 25, preferably 2 to 15 carbon atoms and R_8 is alkyl of 2 to 25 and preferably 2 to 8 carbon atoms, and x is 10 to 100.

The preferred method of preparing the compound used in the present invention, which method is an important aspect of the present invention, is to form a first reaction product by reacting a polyhydroxy compound with a polyisocyanate, then reacting the first reaction product with the acrylic of R_1 in an amount of at least approximately 1 equivalent and leaving at least approximately 1 equivalent of unreacted isocyanate, then this second reaction product is chain extended at the unreacted isocyanate with a polyhydroxy alkylene, sub alkylene, arylene, or sub arylene of R_6 and this third reaction product is then end capped at its chain extended sites with the isocyanatoacrylate of R_1. Preferably the isocyanate and hydroxy reaction compounds are di or tri isocyanate or di or tri hydroxy compounds, more preferably di isocyanate and di hydroxy compound. By equivalent as used in this application it is meant the theoretical reactive potential of the particular group in each molecule.

As a more general description of the method of preparing the preferred embodiments of the new chain extended urethane polyacrylate, first a polyhydroxy compound is reacted with a polyisocyanate forming a first reaction product having about 2 equivalents of reactive isocyanate. This first reaction product is then reacted with less than two equivalents of compound having an acrylic pendent radical and another reactive site preferentially reacting with said first reaction product, forming a second reaction product. Compound as used in the context of this patent application can be made up of compounds of different molecular structure having the recited characteristics or of a quantity of a single molecular structure. The use of the term equivalents (here as stated, less than 2 equivalents) as used in the context of this patent application refers to the reactive potential under the conditions of the recited reaction.

The second reaction product is then reacted with a compound chosen from the group consisting of polyhydroxy alkylene, sub alkylene, arylene, sub arylene, and oxyalkylene or sub oxyalkylene to form a third reaction product. This third reaction product is then reacted with an isocyanato acrylate.

The theoretical reaction forming the first reaction product is a capping of a portion of the reactive isocyanate to form polyurethanes having a radical bridging two urethane groups and leaving other reactive pendent isocyanate reaction sites in the first reaction product. The first reaction product is then reacted with an acrylic compound leaving at least one pendent acrylic radical on at least a substantial portion of the reaction molecular yield of the second reaction product. Because less than the full stoichiometric amount of acrylic compound necessary to satisfy all of the pendent isocyanate is used, substantial pendent isocyanate reaction sites remain. The reacting of the pendent isocyanate reaction sites in the second reaction product with the polyhydroxy compound is understood as a chain extending reaction, at least predominantly capping the pendent reactive isocyanate. Preferably, the first polyhydroxy compound (the one used in forming X) is a dihydroxy oxyalkylene and the second polyhydroxy compound (the residue of which is R_6) is a dihydroxy alkylene and the isocyanato acrylic compound is isocyanato alkylene acrylate.

In another preferred embodiment, the compositions of the present invention are prepared, in general, by forming a first reaction product by reacting a polyhydroxy compound with a polyisocyanate to form a polyurethane. An excess of polyisocyanate is added to form an isocyanate terminated prepolymer. Part of the terminal isocyanate end groups are capped with the acrylic of R_1 and the remainder are chain extended with 1, 4 butanediol. A reaction product of polyisocyanate and an hydroxy acrylate is then reacted with the chain extended prepolymer.

More specifically, there is provided a method for making a compound having the formula:

HMA-(OCN--NCO)-[O-PE-O]-(NCO-NCO)-BD-[OCN--OCN-HMA]

wherein O-PE-O represents hydroxy substituted polyether, polyurethane or polyester,
OCN and NCO represent isocyanate groups and -(OCN-NCO)- represents polyisocyanate,
HMA represents unsaturated hydroxy substituted organic acid ester, and
BD represents lower alkyl diol, comprising sequentially the steps of:

(a) reacting about 1 equivalent of hydroxy substituted oligomer with about 2 equivalents of diisocyanate to form a polyurethane chain having 2 isocyanate end groups

(b) reacting the polyurethane formed in step (a) with about 1/2 equivalent of an unsaturated hydroxy substituted organic acid ester to predominantly form a polyurethane having an isocyanate group on one end and an unsaturated organic acid ester at another end thereof

(c) reacting the product of step (b) with a lower alkyl diol to react with said isocyanate group to form a polyurethane having an unsaturated organic acid ester at one end and a hydroxy at another end thereof

(d) reacting the reaction product of an unsaturated organic acid ester with a diisocyanate with the polyurethane formed in step (c) to from a polyurethane having an unsaturated hydroxysubstituted organic acid ester on at least 2 ends thereof.

In the preferred method, PE is polyether, the polyisocyanate is trimethyl hexamethylene diisocyanate, HMA is hydroxyethylmethacrylate, and BD is butanediol.

As a general proposition suitable polyhydroxy compounds, polyisocyanate compounds and acrylate compounds for use in the present invention are taught by a wide variety of references, including U. S. Patent 4,182,829. Suitable alkyleneisocyanatoacrylate compounds for use in the present invention are taught by U. S. Patent 4,233,425.

The saturated di or tri polyhydroxy compounds which are especially useful in preparing the urethane reaction product X for the practice of the present invention may comprise any of a wide variety of materials especially polyether, polyesters and polycarbonate. Especially preferred are those having substantially no ethylenic unsaturation therein. Thus, one or more materials having two hydroxylic functionalities, which material is not ethylenically unsaturated may be so employed. Preferred materials include aliphatic diols having from 8 to 20 carbon atoms between the hydroxylic functions such as dodecene diol, decane diol, etc. Certain prepolymeric materials, such as the polyalkylene ether glycols are even more preferred. Accordingly, materials such as polymethylene ether glycol, polyethylene ether glycol, polypropylene ether glycol, polybutylene ether glycol, etc. may be so employed. It will be understood by those skilled in the art that a wide variety of such ether glycols may be useful in the practice of the present invention. Preferred materials for use in accordance with the present invention are polybutylene ether gylcol (also called polytetramethylene ether glycol) and polypropylene ether glycol. As will be readily appreciated, the foregoing polyalkylene ether glycols are generally available as mixtures of species having differing molecular weights.

It will be appreciated that a wide variety of polyisocyanates may be employed in preparing the urethane reaction product of X in accordance with the present invention. Exemplary species include the hexamethylene diisocyanate, tetramethylhexamethylene diisocyanate, isophorone diisocyanates, trimer of isophorone diisocyanate and trimer of 1,6 hexamethylene diisocyanate along with many others. It has generally been found most preferred to employ diisocyanate species which are either aliphatic or cycloaliphatic in nature. While such non-aromatic polyisocyanates are preferred, aromatic materials such as toluene diisocyanate and methylene bisphenyl-4-diisocyanate may also be used. The isocyanate functions of the foregoing materials may be viewed as being separated by a number of carbon atoms. Such number of carbon atoms is preferably from 6 to 20. A preferred diisocyanate for use in accordance with the present invention is trimethyhexamethylene diisocyanate.

The glycol is reacted with one or more equivalents of polyisocyanate, preferably diisocyanate, material of this invention in such a fashion as to always have isocyanate functions in excess over glycol functions. The amount of isocyanate moieties to be reacted with the hydroxylic species of the glycol mixture is such that there will be a final stoichiometric excess of isocyanate over hydroxyl. It is preferred that this excess be from 50% to 150% on a molar basis with 75% to 125% being preferred. It is still more preferred that about 100% molar excess of isocyanate be included in excess over the molar amount of hydroxylic functions. The isocyanate moieties are included in excess so as to provide reactive sites for the capping and chain extending of the urethane oligomers with polymerizable acrylic functions.

The acrylates of R_1 of the present invention may be chosen from a variety of compounds in accordance with the present invention. Preferred acrylates are hydroxyalkylation products of acrylic and/or methacrylic acid, such as acrylic acid hydroxyethyl ester, acrylic acid hydroxypropyl ester, methacrylic acid hydroxyethyl ester and methacrylic acid hydroxypropyl ester. The most preferred are the methacrylic acid hydroxyethyl esters.

The second reaction product, which is preferably basically a monoacrylated urethane, is chain extended with additional di or polyhydroxylic compounds or amines chosen from such glycols and amines as the ethylene, propylene, diethylene and butylene glycols. The most preferred chain extender is 1,4 butylene glycol.

The preferred alkyleneisocyanatoacrylate of R_1 may be chosen from a variety of compounds in accordance with the present invention. They are exemplified by such preferred compounds as isocyanatoalkylene methacrylates and the most preferred isocyanatoethylmethacrylate.

In accordance with this invention, the polymerizable oligomers or compounds formed hereby are preferably included in compositions that are dental impression materials for forming impressions of living mammalian tissue to set the impression thereof. The especially preferred compositions are dental impression materials.

The dental impression material composition of the present invention is preferably substantially stable against assuming a permanent remembered form when stored actinic light free. The composition is preferably stable when stored as a single one-component material for a long period of time actinic light free, preferably being stable for at least one month, more preferably three months, and most preferably for six

months or more. By one-component, it is meant that the dental impression material can be stored in the exact form that it will be used by the dentist so that he preferably does not need to do anything other than mold the composition to the surface (surfaces) that is to have its impression made.

The preferred embodiment providing a shelf-stable storable impression material is one having a photoinitiating system. The photoinitiating system may be one of many known in the art to promote polymerization of unsaturated acrylic groups when activated by actinic light of the appropriate wavelengths, strength and length of exposure time. Such systems include, but are not limited to camphoroquinone and other alpha-beta diketones, alone or with reducing agents, such as secondary and tertiary amines; compounds known to catalyze photopolymerization of acrylates upon irradiation by visible light. Materials such as benzoin and benzoin methyl ether which are known to be photopolymerization catalysts utilizing light in the UV portion of the electromagnetic spectrum are operable to cure the presently preferred polymers, but UV light is considered generally undesirable in most instances.

In the aspect of the present invention involving the actinic light activated photopolymerizing composition, the composition is for health and safety reasons preferably one that can be expeditiously cured using light filtered to limit the wave lengths to the visible light range of approximately 360-600 nanometers. More preferably the curing is carried out with the greater portion of the light being within the 400-500 nanometer range.

The amount of photopolymerization initiator or sensitizer and the types are selected with due consideration to the intensity of the light source and the activating wavelength(s) and their own capacity to initiate polymerization. Photoinitiators, for example, camphoroquinone, may be typically used in concentrations between 0.001 and 10% by weight of the polymerizable resin present, preferably between 0.01 and 5%. Accelerators for the photoinitiation for example, tertiary amines, including, for example, methyldiethanolamine, diethanolamine, triethanolamine, 4-ethydimethylaminobenzoate, or 4-dimethylaminobenzonitrile may be used. These are typically used in amounts of between 0.001 and 10% by weight of the polymerizable resin present, preferably between 0.01 and 5%.

Because the urethane polyacrylate (di or tri acrylate) prepolymer that is the preferred compound for use in the dental impression material composition of the present invention is also an independent aspect of the present invention it is pointed out that the urethane polyacrylate polymer can be applied to the preparation of a self-curing dental impression using the more conventional types of curing systems employed in dental impression materials, such as, a paste containing as the initiator, benzoyl peroxide, with fillers such as quartz, talc and silica, a diluent such as polypropylene glycol with a molecular weight, for example, of 4,000 and a stabilizer such as BHT (butylated hydroxy toluene). The base paste would correspondingly contain an accelerator such as dihydroxyethyparatoluidine, a diluent such as polydimethylsiloxane and fillers. By "self-curing" it is meant that a dental impression material, in the form in which it is used, will cure at a predetermined rate due to built-in curing activaters which need no external initiation, such as the actinic light initiation of the more preferred embodiments of the present invention. It is also within the purview of the present invention to provide a self-curing dental impression material with actinic light activated components and thereby obtain a dual cure system that when mixed will cure in the typical self-cure fashion or be accelerated in cure through the use of actinic light.

The impression material can be a viscous liquid, or it can be modified with fillers to result in more viscous pastes or even putties. Such fillers should have suitable optical characteristics in the more preferred embodiments so as not to interfere with the transmission of actinic light through the material in order to permit initiation of the photoinitiator system. The filler particles should have size and surface area appropriate to effect the desired viscosity change.

Generally the non reinforcing fillers are used primarily for viscosity modification and as just filling material are those having a surface area less than 50 square meters per gram (m^2/g), and include calcium carbonate, fused quartz powder, powdered calcium silicaluminate, titanium dioxide, zirconium silicate, aluminum silicate, crystobalite, feldspar, etc. The preferred fillers are silicon dioxide such as fused quartz especially in visible light cured formulations. The fillers may be ground or formed by a variety of means to provide particulate powdered filler of preferred sizes between 0.001 and 100 μm, depending on the application. Particles of individual average sizes of 0.01 and 40 μm are especially preferred.

Reinforcing fillers may also be used in the composition of the present invention. Preferred reinforcing fillers have a surface area of at least 50 square meters per gram and are exemplified by pyrogenically-produced silicon dioxide, silicic acid hydrogels dehydrated so as to maintain their structure, silicon dioxide Aerogels, and precipitated silicon dioxide.

All of these fillers; but especially the reinforcing fillers, can have organosilyl groups on their surface if they have been pretreated, for example, with dimethyl-halogen silanes, or if they have been manufactured; for example by reaction of aqueous silica sol with organo halogensilanes, or have been rendered

hydrophobic in some other way. Mixtures of different fillers can be used. Non-reinforcing fillers may be used at concentrations of at least 20% by weight relative to all of the prepolymers present, whereas reinforcing fillers may be appropriately used in the compound at from 1% to 80% by weight, relative to the total weight of all prepolymers present. Preferred overall filler contents are from 5 to 95%, more preferably 20 to 90%, and most preferably, for some applications, 40 to 85% by weight based on the total composition weight. In the case of actinic light-cured compositions, an important consideration is that the amount and the type of filler is so selected that actinic irradiation may pass through the polymerizable mass in order that polymerization can occur upon irradiation to the depth of the impression but the filler need not match the refractive index of the resins exactly.

Alkyl benzensulfonyl titanates combined with the free radical initiated polymerizable resin, polymerization initiator and the filler, form an important feature of one aspect of the present invention. The preferred alkyl benzensulfonyl titanate is neoalkoxy, tridodecylbenzenesulfonyl titanate (Titanium IV neoalkoxy, tris (dodecylbenzene) sulfonato). It is believed that the titanate gives a better homogeneity by improving the coupling of the filler and the resin. The titanates also are believed to have some accelerating effect in the free radical initiated polymerization of the polymerizable resin even in the low energy visible light initiation of the acrylic cross linking polymerization. The titanate is preferably present in an amount of 0.001 to 2% by weight of the total composition, more preferably 0.005 to 1% and most preferably 0.01 to 0.5%.

Other formulation auxiliaries may also be used. Organic resins, for example PVC powder or methacrylate polymer powder, polyethylene and the like, may be used as suitable extenders and plasticizers. The compositions of the invention may be stabilized by the addition of hydroquinone, catechol, and other similar well-known polymerization inhibitors for the polymerization of (meth) acrylate compounds. Other optional ingredients include pigments and flavoring substances. In one embodiment, for example, the heavy body material may include peppermint flavoring. Still other plasticizers may include, for example, siloxanes, silanes, phthalates, glycerides, and other materials known in the art. Such plasticizers are generally added to alter the hydrophobicity, the softness or hardness of the composition, its viscosity or tackiness, etc. Silane, for example, is a plastcizer which also acts as a binder for the resin and the filler particles.

The dental impression material or composition in the usual situation is preferably non-adhering to tooth enamel, amalgam, composite tooth fillings, metal bridgework, and other substances commonly found in a variety of different patients so that the composition can have relatively universal use. The composition should have the non-adhering ready release characteristic when or after it is changed from its flowable to its remembered or elastic form on being cured. The composition also should not harm soft tissue structure in the mouth of the patient; be substantially non-toxic in use; and not induce allergic reactions of substance in the patient population as a whole. The composition should be easily removed from the soft tissue also and accurately record the soft tissue shape in the permanent elastomeric remembered form of the impression.

The present invention in a preferred embodiment of one of its aspects is the utilization of the new composition of the present invention for application to living mammalian tissue and curing the material in contact with the living mammalian tissue to set the impression thereof. The new composition in a preferred aspect of the present invention in a preferred embodiment is the most preferred use in a method of forming a dental impression in the oral cavity. A composition that is flowable, at least substantially free of memory and capable of assuming a permanent elastomeric memory in response to contact by actinic light, is engaged with the surfaces that are to have their dental impression made. This includes, in a preferred embodiment, forcing a tray of the composition toward the surface until some of the composition flows to assure a good engagement of the composition with the surfaces to be recorded. The tray is preferably maintained in contact with the composition to hold it securely in place and actinic light is passed through at least an integral part of the tray activating the photopolymerizing of the composition to a degree where the composition assumes a permanent elastic-remembered form. It has been found that the impression can be made on a wet surface, i.e. the mouth fluids do not have to be cleaned, without detrimental affect.

A preferred tray passes actinic light through all of its mass to the composition. For this purpose the tray may be a clear plastic.

In its preferred form, the method includes aspects of the materials that can perform the needed actions for preferred performance of the preferred methods of the present invention. The preferred method does not require pre-mixing of the composition before it is used. The compositions are preferably flowable, deformable and substantially free of any shape memory prior to activation by actinic light so that the composition can be formed to the dental impression including the adjacent soft tissue surfaces of the oral cavity. The preferred composition assumes a permanent elastomeric-remembered form in response to actinic light exposure. By permanent elastomeric-remembered form it is meant that the dental impression material can be stripped from the teeth by stretching and deforming in response to pressure applied by, in

the usual usage the human hand, to pull the material off the teeth while retaining the remembered shape of the teeth in detail.

The one-component composition of the present invention can be packaged in various ways including being preloaded into a syringe, from which the dentist can express the material directly onto the soft or hard tissues to be reproduced. The composition can also be preloaded into a dental impression tray which can be placed by the dentist directly into the mouth of the patient or can be preloaded into a collapsible tube from which the dentist can squeeze the material into a dental impression tray which passes actinic light prior to placement in the patient's mouth. An important point is that the container or its overwrap be metal or otherwise opaque to actinic light or be packaged in such a manner as to protect the composition of the invention from actinic light prior to use by the dentist.

In a preferred embodiment of the present invention, the dentist places the special tray filled with the composition of the present invention in the mouth of the patient in such a way that the impression material fully contacts the entire area of the oral tissues of which an impression is being made. An optional step may be taken by the dentist prior to placing the filled tray in the patient's mouth in order to avoid entrapping air bubbles at the tissue surface; or in constricted areas, the dentist would coat the surface of the tissues; especially constricted areas such as between teeth, with a more fluid impression material of the present invention preferably by extrusion from a syringe and then place the filled tray as described above.

After placement of the special tray, polymerization of the impression material is initiated with actinic light and polymerized preferably within 5 minutes, more preferably within 2 minutes and most preferably within 1 minute or less. The actinic light is preferably visible light from a source such as the PRISMETICS® lite polymerization units of The L.D. Caulk Company, which produces visible light with a band of wavelengths between 400 and 500 nanometers and an energy output of approximately 550 milliwatts per square centimeter from the tip of the unit's light guide. The polymerization time can vary depending on the intensity and wavelength of the light used, the quantity of material to be polymerized and the tray used. For example, the tray could be a special tray of the construction described below.

The time required for the dentist and the patient to wait for polymerization or setting of the shape to take place may be reduced from 8 - 10 minutes down to two minutes or less, and the total time required for placement and curing of the one-component impression material of the present invention may be reduced to 2-3 minutes, as compared to approximately 15 minutes in conventional techniques which require mixing of two-component impression materials.

The impression tray to be used with the composition of the present invention must be capable of transmitting light to all areas of the impression material that are to be activated directly by the actinic light. One simple construction would be simply a standard transparent plastic tray whereby polymerizing light can be directed through all portions of the base of the tray onto the material inside the tray.

A suitable tray is the subject of United States patent Number 4,553,936
This tray has a light-guide means such as a short solid light pipe rod at the anterior portion of a transparent tray which transmits light from the light source to the tray. The light is then transmitted to the impression material by the body of the tray itself. The light may be reflected or deflected directly into the material by a reflective tray surface. Such reflective surfaces are provided by metallized mirror-like coatings on the outer tray surface, or by geometric shaped facets, grooves or ridges which reflect or deflect light at roughly 90° from the general surface of the tray. The facets, grooves or ridges occur either on the outer or inner tray surfaces.

A special impression tray could be prefilled with impression material and be wrapped entirely with a metal foil-plastic laminate material to be opened at an area allowing for the taking of the impression only at the time of use, which would prevent the impression material from being exposed to light before use. The metal foil could serve the dual function of preventing unintentional light exposure and subsequently providing a reflecting surface for the light supplied to the tray to bring about polymerization.

The impression material of the invention has been found to be suitable for adding on. For example, if the impression material is not completely cured, or if an insufficiant quantity of material has been dispensed on the tray, a partial impression or incompletely cured impression may be removed from the mouth, light body impression material may be added to the tray and/or the teeth, and the impression can then be completed. The bond between the impression material in the tray and the impression material added on is homogeneous and complete.

The preferred materials of the present invention have special applications in dentistry in addition to their most preferred application in preparing dental impressions. By dental impressions it is meant, reverse images of dental features in the mouth to serve as molds from which dental prosthesis can be prepared or models for preparing dental prosthesis can be prepared. The preferred materials of the present invention also have application in methods of directly preparing dental prosthesis by which term it is meant to include

parts of dental prosthesis. This provides the format for an entirely new method of preparing dental prosthesis. A particularly preferred aspect of the present invention is the preparing of dental prosthesis by relining of dentures that are either damaged or no longer fit properly and/or comfortably.

The material is relatively soft and plastic so that it conforms with the contours of the gums, but is relatively substantial and durable so that it stays in place, retains its shape, and stays soft and pliable and does not break-up when the stresses of mastication are encountered.

The dentist would take a removable denture which is no longer fitting comfortably in a patient's mouth and apply to all of the areas of the denture which contact the patient's soft tissue, a thin coating of one of the compositions of the present invention. The dentist would then insert the denture into the patient's mouth and engage the composition while it is flowable and at least substantially free of memory with the surfaces in the oral cavity that are to be reproduced as the new closely fitting negative dental prosthetic part of the surface. The denture is pushed firmly into place, forcing the composition against the patient's dental surface until some of the composition flows into good conformity with the surface to form the composition into an accurate negative impression of the oral surface. The denture is then removed from the patient's mouth and, when a preferred actinic light-cured embodiment of the present invention is used, cured by photoinitiation with actinic light. Acrylic dentures have been found to lend themselves to a preliminary curing sufficient to secure the liner to the denture and establlish shape using the PRISMETICS® lite.

The characteristics of the preferred light have already been described with respect to the actinic light initiation of the preferred impression material embodiments of the present invention. A very effective procedure would be to insert the denture into a TRIAD® light-curing unit (a product of Dentsply International Inc.) wherein actinic light would be impinged on the negative impression formed composition by operation of the unit. This photopolymerizes the composition to a degree that the composition assumes a permanent elastomeric remembered form of the negative of the oral surface.

It will be understood that the flowable composition is carried on the surface of the removable denture that is to be juxtaposed against the soft tissue in the oral cavity when said composition is forced toward the soft tissue surface. The actinic light, except for ambient light, is preferably substantially limited to the visible light spectrum of about 360 to about 600 nanometers. If, on reinsertion, everything is not as desired, adjustment can be easily made by stripping off the reline prosthesis or cutting out a portion of it and repeating the forming process directly to the soft tissue as described.

The composition of the present invention in its actinic light-cured form is preferably substantially stable against assuming a permanent remembered form when stored actinic light free. The composition is preferably non-toxic in use in the oral cavity; stable in storage for at least one month as a one-component composition when actinic light free; and assumes a permanent elastomeric memory when exposed to light filtered to limited wavelengths within the visible light range for one minute to a depth of 2,54 cm (one inch).

It has been found that the polymer made according to the invention is suitable for use in a number of applications. For example, when using lower molecular weight materials, to provide for a rigid structure, the polymer of the invention can be used to make a personalized mouthguard (for sports) or nightguard (to prevent grinding of teeth). The mouthguard or nightguard can be made in much the same manner as a dental impression. That is, the polymer may be placed in the mouth to obtain an impression of the general features of the mouth, and the polymer can then be light cured in the mouth or removed from the mouth and cured.

It has been found that although the polymeric material is hydrophilic, it does not absorb excessive amounts of water and therefore can be used in the mouth for an extended period of time when used as, for example, a soft denture liner or mouthgaurd.

As will be apparent to those skilled in the art, the polymer of the invention can also be used to stabilize dental equipment in the mouth; as a tissue conditioner medicament carrier used to treat the soft tissue in the mouth; as a rubber dam clamp sealer; a hemastatic retractor; impression material for removable prosthodontics; material to secure matrix bands and wedges in restorative procedures; medical wound dressing material; as a substitute for epoxy molds; as a pipe sealer (for example, for PVC); as an oral dressing over implants after re-entry to place post and cores; as a protective covering over ortho brackets to prevent or minimize trauma; as translucent, intraoral or direct, stint for pontics or temporaries; for making impressions for hearing aids; and for prosthetics, especially for facial use.

Other uses inside and outside dentistry will be readily apparent to those skilled in the art.

The impression material may be loaded immediately prior to use or in the factory with substances or medicaments that can be used to treat or reduce pain in the gums. For example anti-inflammatory agents, anti-bacterial agents or astringents such as aluminum chloride or epinephrine, and others may be used as needed.

The invention is further illustrated by the following examples:

EXAMPLE 1 (Reference)

A preferred isosyanatoethyl methacrylate urethane methacrylate oligomer elastomeric prepolymer compound was prepared according to the following formulation:

Polypropylene glycol MW-2,000 Voranol 2120 (Dow Chemical)	690 g
Trimethyl hexamethylene diisocyanate (Thorson)	145 g
Dibutyl tin dilaureate	0.4170 g
Hydroxyethylmethacrylate (HEMA) (Esschem)	50.0 g
1,4 Butane diol (BASF)	31.0 g
Isocyanatoethyl methacrylate (Dow Chemical)	53.4 g

The procedure was as follows:

One mole of polypropylene glycol (2 equivalents of hydroxy) are reacted with two moles of trimethyl hexamethylene diisocyanate (4 equivalents of isocyanate) employing the dibutyl tin dilaureate.

The polypropylene glycol was dewatered with molecular sieve (4A) for two days. Then it was charged into a 2 liter reactor. Stirring and dry air flow through the reactor was begun. The dibutyl tin dilaureate was added to the glycol dropwise and allowed to stir in. Then the trimethyl hexamethylene diisocyanate was added to the glycol-catalyst mixture dropwise using a separatory funnel. The addition was done at room temperature and The drop rate was controlled to keep the temperature below 50C. After about three hours, all the diisocyanate had been added. The mixture was allowed to stir overnight with a heating mantle up around the reactor (no heat turned on). The next day 45 grams HEMA was added dropwise, again controlling the drop rate to keep the pot temperature below 50C. After all the HEMA was added, the 1,4 Butane diol was added dropwise to the reactor contents. This mixture was allowed to stir overnight. The next day, isocyanatoethyl methacrylate was added dropwise through the separatory funnel and stirred in. A slight excess of HEMA (5 grams) was finally added to the pot about three hours after the final addition of isocyanatoethyl methacrylate to be sure all the free isocyanate was reacted. The pot contents were allowed to stir for 24 hours and then unloaded.

EXAMPLE 2 (Reference)

A dental impression forming composition was compounded by hand mixing the following formulation at ambient conditions.

Resin of EXAMPLE 1	100 parts by wt.
Camphoroquinone	0.15 parts by wt.
Methyl diethanol amine (MDEA)	0.5 parts by wt.

The dental impression forming composition was then tested for its relevant characteristics with the following results:

The composition was irradiated with a 500 watt General Electric Photo-EBV photoflood lamp containing light from the visible light spectrum for 5 minutes with the lamp approximately 2 inches from the dental impression forming composition specimen. The material cured to an elastic solid. The following testing results were obtained using ADA Spec 19 (1984) for non-aqueous elastomeric impression materials when the cured dental impression composition cured by irradiation as described was tested:

Compression Set (%)	Strain (%)	Dimensional Change (%)
0.65	3.75	24 hrs 0.23 expansion 1 wk 0.27 expansion

EXAMPLE 3 (Reference)

A dental impression forming composition was compounded by hand mixing the following two formulations separately at ambient conditions.

The catalyst paste was prepared according to the following formulation:

1. resin	52.05 parts by wt.
2. benzoyl peroxide	1.04 parts by wt.
3. filler	27.33 parts by wt.
4. polypropylene glycol (MW 4,000)	19.52 parts by wt.
5. BHT (butylated hydroxy toluene)	0.06 parts by wt.

A base paste was prepared according to the following formulation:

1. resin	51.80 parts by wt.
2. dihydroxy ethyl p-toluidine	0.93 parts by wt.
3. filler	27.20 parts by wt.
4. polypropylene glycol (MW 4,000)	19.43 parts by wt.

The two pastes were mixed at an equal weight ratio by spatulating on a parchment pad for approximately 45 seconds. The material cured to an elastic solid with a shore A hardness of about 55 (ASTM 19, 1984 testing method) in 6 minutes at ambient temperature.

Below are the results of testing this material in accordance with ADA Spec 19 referred to in Example 2:

Dimensional Change %	Mix(mm) Consistency	Compression Set (%)	Strain (%)	Flow (%)
24 hrs. 0.17 1 wk. 0.18	49	0.5 - 0.6	2.5 -3.5	0.10

The material was determined to be compatible with gypsum and detailed reproduction was fine when tested in accordance with ADA Specification 19 for non-aqueous elastomeric materials.

EXAMPLE-4

Another preferred isocyanatoethyl methacrylate urethane methacrylate oligomer elastomer prepolymer compound was prepared according to the following formulation

Polypropylene glycol (MW 4000) Voranol 2140 (Dow Chemical)	834.6g
Trimethylhexamethylene diisocyanate (Thorson Chemicals)	87.7g
Stannous octoate	0.50g
Hydroxyethyl methacrylate (Rohm & Haus)	27.1g
1,4 Butanediol (BASF)	18.7g
Isocyanatoethyl methacrylate	30.8g

The procedure was as follows:

In theory, one mole of polypropylene glycol (2 equivalents of hydroxy) are reacted with two moles of trimethylhexamethylene diisocyanate (4 equivalents of isocyanate) employing the stannous octoate as catalyst.

The polypropylene glycol was charged into a 2 liter reacter. Stirring and dry air flow through the reactor was begun. The stannous octoate was charged to the reactor and allowed to stir in. Then the trimethylhexamethylene diisocyanate was added to the glycol catalyst mixture dropwise using a separatory funnel. The addition was done at room temperature and was controlled to keep the temperature below 50 °C. Addition was complete after 30 minutes. The contents were allowed to stir for 30 minutes more. Samples were taken and titration was done to determine isocyanate content. Isocyanate was found to be 1.9% which indicated complete reaction of the polypropylene glycol and trimethyhexamethylene diisocyanate. Then the 27.1 grams of HEMA were added all at once to the reactor contents which were at a temperature of about 40 °C. The contents were allowed to stir for 45 minutes. Then titration samples were taken and the socyanate

content determined to be 0.95%. This indicated complete reaction of the HEMA with the isocyanate terminated prepolymer leaving 1 equivalent of isocyanate sites for reaction with 1,4 butane diol. At this point 18.7 grams of 1,4 butane diol were added to reactor contents all at once and allowed to stir in for 2 hours. The temperature of the reactor continued between 40 and 50 °C for this procedure. At the end of 2 hours the isocyanatoethyl methacrylate was added dropwise to the reactor using a separatory funnel. This addition took approximately 30 minutes. Stirring was continuous until the next morning to be sure all the free isocyanate was reacted. Then the pot contents were unloaded.

EXAMPLE-5

A dental impression forming composition was compounded by hand mixing the following formulation at ambient conditions.

Resin of EXAMPLE 4	12.27g
Camphorquinone	0.031g
4-Ethyldimethylaminobenzoate	0.200g
Butylated hydroxy toluene	0.025g
Crystobalite filler	9.83g
fumed silica (Aerosil R-972 from Degussa)	1.75g
blue pigment (Dayglo)	0.035g
Alkyl benzl phtbalate	0.88g

The composition was irradiated for 2 minutes with a 500 watt GE Photoflood lamp containing light from the visible light spectrum with the lamp approximately 2 inches from the dental impression forming composition specimen. The material cured to an elastic solid.

EXAMPLE-6

A dental impression forming composition was compounded by hand mixing the following formulation at ambient conditions:

Resin of EXAMPLE 4	39.0g
Di (C_{7-9-11} Alkyl) Phthalate (Palatinol 711 P from BASF)	1.60g
Peppermint Oil	0.20g
Titanium IV neoalkoxy, tris (dodecylbenzene) sulfanato (Ken React LICA 09 from Kenrich Petrochemicals, Inc.)	0.20g
fumed silica (Aerosil R-972 from Degussa)	4.20g
blue pigment (Dayglo)	0.080g
Feldspar	35.5g
Camphorquinone	0.10g
4 Dimethylaminobenzonitrile	0.24g

The composition was irradiated for 1 minute using the photoflood lamp procedure of Example 2. The material cured to a elastic solid.

The depth of cure was tested using the Presmetics® light earlier described. A sample of material 20 mm thick was covered with a sheet of clear Mylar about 1 mil thick. The sheet was in direct contact with the sample. The light was directly engaged against the sheet of Mylar. The light was on 10 seconds. Curing was to a depth of 8 mm as determined by wiping away the uncured material from the bottom of the sample and measuring the remaining cured material.

EXAMPLE-7

A dental impression forming compound of the following formulation was compounded by a double planetary mixer at reduced pressure:

Resin of EXAMPLE 4	45.98g
Camphorquinone	0.09g
4-Dimethylaminobenzonitrile	0.4g
Butylated Hydroxy Toluene	0.05g
Di (C_{7-9-11} Alkyl) Phthalate (Palatinol 711 P from BASF)	2.0g
Titanium IV neoalkoxy, tris (dodecylbenzene) sulfanato (as in Example 6)	0.25g
Fused Quartz	43.6g
fumed silica (as in Example 6)	7.6g
green pigment (Dayglo)	0.10g
blue pigment (Dayglo)	0.02g

The composition was irradiated for 40 seconds using the photoflood lamp procedure of Example 2. The material cured to a rubbery solid.

The depth of cure test procedure of Example 6 was preformed and the depth of cure was 13 to 14 mm. The material gave the following physical properties as tested by ADA Spec. #19 referred to in Example 2:

Compression Set	Strain	Dimensional Change	Detail Reproduction	Flow
1%	2.6%	0.05%	20 micron line	0.10%

EXAMPLE-8

The procedure of Example 7 was repeated except the formula was as follows:

Resin of EXAMPLE 4	39.64g
Camphorquinone	0.08g
4-Ethyldimethylaminobenzoate	0.24g
Butylated hydroxy toluene	0.04g
Di (C_{7-9-11} Alkyl) Phthalate (as in EXAMPLE 6)	2.0g
Titanium IV neoalkoxy, tris (dodecylbenzene) sulfonato (as in EXAMPLE 6)	0.25g
Fused Quartz	43.74g
fumed silica (as in EXAMPLE 6)	14.0g
blue pigment (Dayglo)	0.07g

The composition was irradiated using the procedure of Example 7. The material cured to a stiff, but rubbery solid and gave the following physical properties as tested by ADA Spec #19 referred to in Example 2:

Compression Set	Strain	Dimensional Change	Detail Reproduction	Flow
0.85%	1.8%	N/A	20 micron line	N/A

EXAMPLE-9

A dental impression forming compound of the following formulation was compounded by a double planetary mixer at reduced pressure:

Resin of EXAMPLE 4	390.41g
Camphorquinone	0.79g
Butylated Hydroxy Toluene	0.170g
4-Dimethylaminobenzonitrits	3.63g
Fused Quartz of EXAMPLE 7	437.3g
Magenta Pigment (Dayglo)	0.80g
fumed silica (as in EXAMPLE 6)	139.9g
gamma-Methacryloxypropyltrimethoxysilane	5.00g
Di (C_{7-9-11} Alkyl) Phthalate (as in EXAMPLE 6)	19.50g
Titanium IV neoalkoxy, tris (dodecylbenzene) sulfonato (as in EXAMPLE 6)	2.50g

The composition was tested for depth of cure using the procedure of example 6 and gave results of 19-20 mm. The composition was irradiated for 40 seconds with a Prismetics lite using the wide tip with the tip directly above the dental impression forming composition specimen using a Mylar spacer. The material cured to a rubbery solid and gave the following physical properties as tested by ADA Spec. #19 referred to in Example 2:

Impression Set	Strain	Dimensional Change	Detail Reproduction
0.60%	1.1%	0.02%	20 micron line

EXAMPLE 10

A syringeable viscosity dental impression forming compound of the following formulation was compounded in a double planetary mixer at reduced pressures:

Resin of EXAMPLE 4	456.1g
Camphorquinone	0.92g
Butylated Hydroxy Toluene	0.20g
4-Dimethylaminobenzonitrile	2.81g
Blue pigment (Dayglo)	2.514g
Fused Quartz of EXAMPLE 7	434.6g
fumed silica (as in EXAMPLE 6)	75.9g
Di (C_{7-9-11} Alkyl) Phthalate (as in EXAMPLE 6)	19.5g
Titanium IV neoalkoxy, tris (dodecylbenzene) sulfonato (as in EXAMPLE 6)	2.50g
gamma-Methacryloxypropyltrimethoxysilane	5.00g

The composition was tested for depth of cure using the procedure of example 6 and gave results of 15 to 16 mm. The composition was irradiated for 40 seconds with a Prismetics lite using the wide tip with the tip directly above the dental impression forming composition specimen using a Mylar spacer. The material cured to a rubbery solid and gave the following physical properties as tested by ADA Spec. #19 referred to in Example 2:

Compression Set	Strain	Detail Reproduction	Dimensional Change
0.72%	1.9%	20 micronline	0.04%

Example 11

Voranol 2120 (polypropylene glycol) (MW 2000)	68.25%
TMDI (Trimethylhexamethylene diisocyanate)	14.34%
Stannous Octoate	0.05%
HEMA (Hydroxyethyl methacrylate)	3.14%
1,4 - Butanediol	4.29%
TIM (Reaction product of TMDI and HEMA)	8.10%
HEMA	1.82%
Phosphoric Acid - Water Solution (1:1)	0.0021%

The polypropylene glycol (Voranol 2120) with an average molecular weight of 2000 is first mixed with the phosphoric acid solution. This neutralizes residual base in the polypropylene glycol which can act as a catalyst in the prepolymer reaction with TMDI. Then the stannous octoate is added as the catalyst for urethane formation. A 2/1 excess of TMDI is added to form an isocyanate terminated prepolymer. Then part of the residual isocyanate is capped with HEMA. The remainder is chain extended with 1,4-Butanediol. Then TIM is added. TIM is the reaction product of 1 mole (2 equivalents) of TMDI and 1 mole (1 equivalent) of HEMA. It has one free isocyanate end and one methacrylate end when the reaction is complete. The isocyanate portion reacts with the remaining hydroxyl group from 1,4-Butanediol. Finally, a small amount of HEMA is added to react any residual isocyanate.

A comparison of moles and equivalents of the ingredients is seen below:

	Moles	Equivalents
Voranol 2120	1	2
TMDI	2	4
HEMA	0.7	0.7
1,4-Butanediol	1.4	2.8
TIM	0.7	0.7
HEMA	0.4	0.4

Activated Resin	
Resin described above	98.78%
Camphorquinone	0.20%
4-Dimethylaminobenzonitrile	0.92%
Butylated Hydroxy Toluene (BHT)	0.10%

Heavy Body Tray Material	
Activated Resin described above	45.95%
Fused Quartz (average particle size 15-25 microns)	42.37%
Aerosil R-972 fumed silica	9.04%
Dayglo A-21 Corona Magenta pigment	0.0824%
Palatinol 711P (Di-C_{7-9-11}) Alkyl Phthalate	2.00%
Ken React LICA 09	0.05%
Gamma-Methacryloxypropyltrimethoxysilane	0.50%

Light Body Syringeable Material	
Activated resin described previously	54.76%
Fused Quartz (average particle size 15-25 microns)	39.68%
Aerosil R-972 fumed silica	1.55%
Dayglo A-19 Horizon Blue pigment	0.25%
Palatinol 711P (Di-C_{7-9-11}) Alkyl Phthalate	3.10%
Ken React LICA 09	0.13%
Gamma-Methacryloxpropyltrimethoxysilane	0.52%

The attached table provides a comparison of the properties of the material of this example as compared with ADA specs.

The material with either resin has the advantages of unlimited work time, no mixing, command cure, and a fast cure. Furthermore, the impression has good readability, is hydrophilic, and can be poured up immediately in gypsum or epoxy.

In a preferred embodiment, peppermint may be added to the heavy body material.

Material of Example 11

Properties	Heavy Body Tray Material	Light Body Syringeable Material	ADA Spec. 19
Work Time	Unlimited in black storage. In ambient light material is workable for 4' to 5'	Unlimited in black storage. In ambient light material is workable for 4' to 5'	Minimum 2'00"
Set Time	Immediately after light cure	Immediately after light cure	Maximum 10'00"
Depth of Cure (mm)	20	20	--
Compression Set (%)	1.4	1.1	Maximum 2.5
Strain (%)	2.1	5.4	2.0 - 20.0
Dimensional Change (%)	0.25	0.20	Maximum 0.5
Detail Reproduction	20 micron line	20 micron line	20 micron line
Compatibility Gypsum	Yes	Yes	Yes
Copper Metalizing Bath	Yes	Yes	Yes
Silver Metalizing Bath	Yes	Yes	Yes

EXAMPLE 12

The resin of example 11 was compounded into heavy body and light body impression pastes under reduced pressures according to the formulas below:

Heavy Body Tray Material	
Resin of EXAMPLE 11	45.31%
Camphorquinone	0.092%
4-Dimethylaminobenzonitrile	0.422%
Butylated Hydroxy Toluene	0.0459%
Ground Fused Quartz (average particle size 15-25 microns)	43.72%
Aerosil R-972 fumed silica	7.50%
Dayglo Corona Magenta colorant	0.082%
Palatinol 711P (Di C_{7-9-11} Alkyl Phthalate)	2.00%
Peppermint Oil	0.20%
Ken React LICA 09	0.10%
gamma - Methacryloxypropyltrimethoxysilane	0.50%

Light Body Syringeable Material	
Resin of EXAMPLE 11	55.23%
Camphorquinone	0.11%
4-Dimethylaminobenzonitrile	0.51%
Butylated Hydroxy Toluene	0.11%
Ground Fused Quartz (average particle size 15-25 microns)	37.63%
Aerosil R-972 fumed silica	2.42%
Dayglo Horizon Blue colorant	0.25%
Palatinol 711P (Di-C_{7-9-11} Alkyl Phthalate	3.10%
Ken React LICA 09	0.13%
gamma - Methacryloxypropyltrimethoxysilane	0.50%

EXAMPLE 13

An isocyanatoethyl methacrylate urethane methacrylate oligomer elastomer prepolymer compound was prepared according to the formulation and procedure of EXAMPLE 4. This resin was then compounded according to the formula below under reduced pressure:

Resin of EXAMPLE 4	46.05%
Camphorquinone	0.093%
4-Dimethylaminobenzonitrile	0.279%
Butylated Hydroxy Toluene	0.046%
Silanated Fused Quartz	43.54%
Fumed Silica (Aerosil R-972)	7.563%
Dayglo blue pigment	0.067%
Di(C_{7-9-11} Alkyl) Phthalate (Palatinol 711P from BASF)	1.96%
Peppermint Oil	0.15%
Titanium IV neoalkoxy, tris (dodecylbenzene) sulfonato (as in EXAMPLE 6)	0.25%

Three Dimensional change specimens of the above material were made in the recommended ADA Spec 19 mold by filling and curing 1 minute under the photoflood lamp of EXAMPLE 2. After curing the specimens were demolded and readings of the length of the lines were taken according to ADA Spec. 19. After this immediate reading the specimens were each immersed in 250 ml of deionized water and stored at 37 °C. Periodically, the specimens were removed and readings of the ruled line length were taken and

recorded. The percentage of change was calculated and is shown in the table below illustrating the dimensional stability of the material with time in a wet environment:

Average % Dimensional Change 1 week	Average % Dimensional Change 1 month	Average % Dimensional Change 3 months	Average % Dimensional Change 16 months
+0.34% expansion from immediate reading	+0.31% expansion from immediate reading	+0.31% expansion from immediate reading	+0.19% expansion from immediate reading

Furthermore, the material was noted to be soft and pliable throughout the period of 16 months in the water.

EXAMPLE 14

A non-staining VLC soft denture liner was prepared according to the followong procedures:

A heavy paste 1 was made in a double planetary mixer under reduced pressure using the resin of Example 11 according to the formula below.

Resin of EXAMPLE 11	45.36%
Camphorquinone	0.092%
4-Dimethylaminobenzonitrile	0.422%
Butylated Hydroxy Toluene	0.046%
Ground fused quartz (mean particle size 15-25 microns)	42.37%
Fumed Silica (aerosil R-972)	9.04%
Dayglo Corona Magenta	0.082%
Palatinol 711P	2.00%
gamma-Methacryloxypropyltrimethoxy silane	0.50%
Ken React LICA 09	0.1%

A paste 2 was made by hand using silicone methacrylate resin according to the formula below:

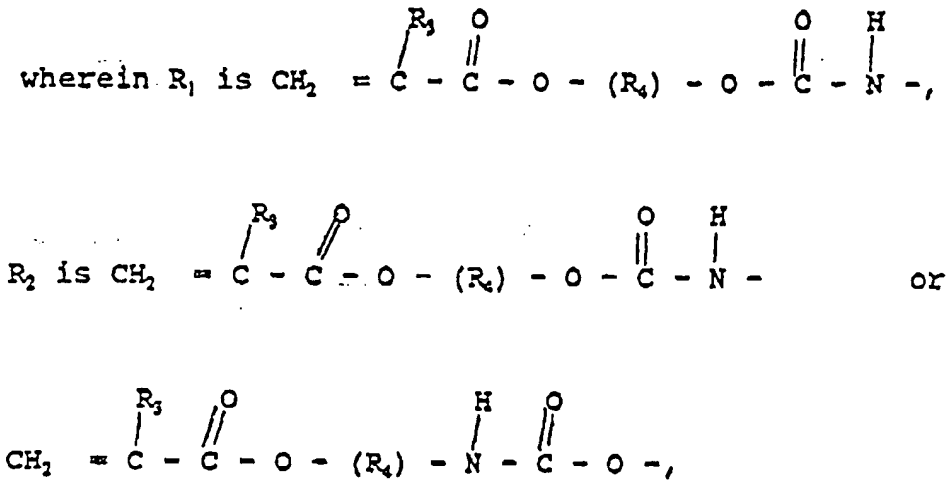
Silicone Methacrylate Resin (P5X2294 from Petrarch Systems, Inc.)	45.37%
4-Dimethylaminobenzonitrile	0.42%
Camphorquinone	0.092%
Butylated Hydroxy Toluene	0.023%
Ground Fused Quartz (mean particle size 15-25 microns)	42.37%
Fumed silica (Aerosil R-972)	9.04%
Dayglo Corona Magenta	0.080%
Ken React LICA 09	0.10%
Palatinol 711P	2.00%
gamma-Methacryloxypropyltrimethoxysilane	0.50%

Then, 25 parts of Paste 1 was mixed by hand with 25 parts of Paste 2 to give Paste 3. Discs of Pastes 1, 2, and 3 were made in 3 mm x 20 mm stainless steel rings and cured under a Photoflood lamp for 30 seconds. Then these specimens were placed in coffee and tea for 24 hours at 37 • C. After removal from the coffee and tea the discs were rinsed and blotted dry. the specimens were examined visually for staining. Paste 1 was severely stained. Paste 3 had slight to moderate staining. Paste 2 was the best with minor staining. Upon examination of the discs, it was found that Paste 3 appeared to have the best combination of reduced staining and elastomeric properties. Paste 2 was too rigid and brittle when cured to be a good soft denture liner.

Claims

1. An elastomeric dental impression material composition for use in dentistry comprising a compound of the general formula

$R_1 - (A) - R_2$



wherein R_1 is $CH_2 = C(R_3) - C(=O) - O - (R_4) - O - C(=O) - N(H) -$,

R_2 is $CH_2 = C(R_3) - C(=O) - O - (R_4) - O - C(=O) - N(H) -$ or

$CH_2 = C(R_3) - C(=O) - O - (R_4) - N(H) - C(=O) - O -$,

R_3 is H, alkyl of 2-10 carbons, substituted alkyl of 2-10 carbons, aryl of 6-14 carbons, substituted aryl of 6-14 carbons, F, or CN and R_3 may be the same or different in each position;

R_4 is a divalent hydrocarbon radical or divalent substituted hydrocarbon radical and may be straight or branched chain or cyclic or a combination thereof from 2-10 carbons; and

A is a polyurethane, polyether or polyester group;

from 5 to 95 percent by weight fillers and a photoinitiator, wherein substituted represents a chemical substituant selected from the group consisting of halogen, lower alkyl having from 1 to 6 carbon atoms, oxy lower alkyl having from 1 to 6 carbon atoms, silyl lower alkyl having from 1 to 6 carbon atoms, phenyl, halophenyl, alkoxyphenyl, trihalomethyl and dihalomethyl having from 1 to 6 carbon atoms, and wherein said composition has a molecular weight of 500-4000 and a viscosity suitable for use as an oral bandage or a dental impression material and is non-toxic in use in the oral cavity, stable in storage for at least one (1) month as a one-component composition when actinic light free, and assumes a permanent elastomeric memory suitable for use as an oral bandage or a dental impression material when exposed to light filtered to limited wavelengths substantially within the visible light range for one (1) minute to a depth of 2.54 cm (one (1) inch).

2. An impression material for application to mammalian tissue and curing in contact therewith to set the impression thereof; said impression material comprising free radical initiated polymerizable resin present in an amount of 5 to 95% by weight of the total composition; alkyl benzensulfonyl titanate present in an amount of 0.001 to 2% by weight of the total composition; a polymerization initiator present in an amount of 0.001 to 10% by weight of polymerizable resin; and filler present in an amount of 5 to 95% by weight of the total composition, wherein said polymerizable resin comprises a compound of the formula R_1-(A)-R_2 as defined in Claim 1.

3. The impression material of Claim 2 wherein said free radical initiated polymerizable resin is present in an amount of about 10 to 80% by weight of the total composition; said alkyl benzensulfonyl titanate is neoalkoxy; (diallyl) oxy tri (dodecyl) benzenesulfonyl titanate and is present in an amount of 0.005 to 1% by weight of the total composition; said polymerization initiator is present in an amount of 0.01 to 5% by weight of polymerizable resin; and filler is present in an amount of 20 to 90% by weight of the total composition.

4. A composition according to Claim 1 for use as a soft denture liner comprising a compound of the general formula:

$R_1 - (A) - R_2$

wherein R_1 is $CH_2 = C(R_3) - C(=O) - O - (R_4) - O - C(=O) - N(H) -$

and R_2 is as defined in Claim 1,

R_3 is H, alkyl, of 2-10 carbons, substituted alkyl of 2-10 carbons, aryl of 6-14 carbons, substituted aryl of 6-14 carbons, F or CN and R_3 may be the same or different in each position

R_4 is a divalent hydrocarbon radical or divalent substituted hydrocarbon radical and may be straight or branched chain or cyclic or a combination thereof having from 2-10 carbons and

A is a polyurethane, polyether or polyester group, from 5 to 95 percent by weight fillers and a photoinitiator, wherein substituted represents a chemical substituent selected from the group consisting of halogen, lower alkyl having from 1 to 6 carbon atoms, oxy lower alkyl having from 1 to 6 carbon atoms, silyl lower alkyl having from 1 to 6 carbon atoms, phenyl, halophenyl, alkoxyphenyl, trihalomethyl and dihalomethyl having from 1 to 6 carbon atoms, and wherein said composition has a molecular weight of 500-4000 and a viscosity suitable for use as a soft denture liner and is non-toxic in use in the oral cavity, stable in storage for at least one (1) month as a one-component composition when actinic light free, and assumes a permanent elastomeric memory suitable for use as a soft denture liner when exposed to light filtered to limited wavelengths substantially within the visible light range for one (1) minute to a depth of 2.54 cm (one (1) inch).

5. The soft denture liner of claim 4 in which (A) is

$$R-N(H)-C(=O)-O-(CH_2)_4-O-C(=O)-N(H)-R-N(H)-C(=O)-O-(R_3-O)-C(=O)-N(H)-R-$$

or

$$(CH_2)_4-O-C(=O)-N(H)-R-N(H)-C(=O)-O-(R_3-O)_x-C(=O)-N(H)-R-$$

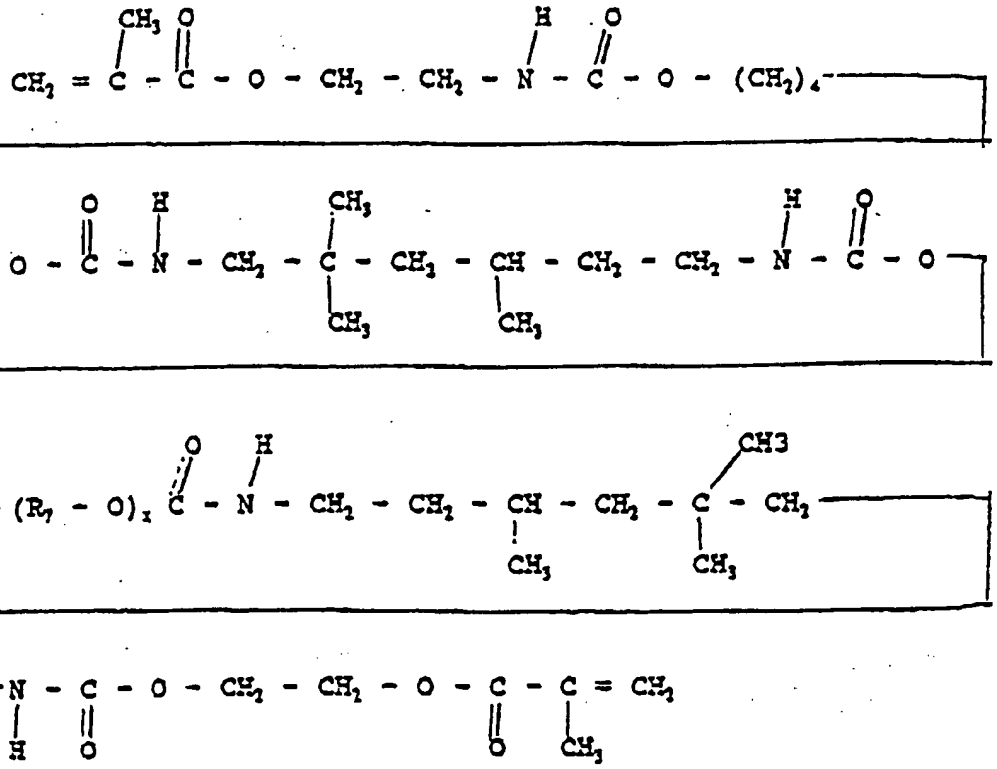
where R is alkyl of 2 to 25 carbons, R_8 is alkyl of 2 to 25 carbons, and x is 10 to 100.

6. The soft denture line of claim 5 in which the new composition or matter of claim 1 wherein said compounds provides that general formula

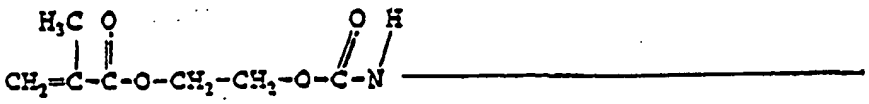
A is (R_5)- X -(R_6)

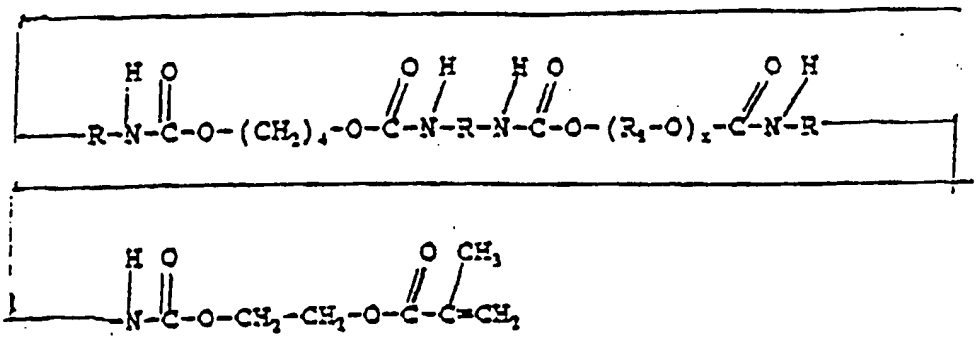
R_5 and R_6 are each divalent hydrocarbon radicals or divalent substituted hydrocarbon radicals, X is a polyurethane, polyether, or polyester and R_5-X and R_6-X are joined by a urethane linkage and R_5 and R_6 have from 2 to 100 carbons.

7. The soft denture liner of claim 6 comprising a compound of the general formula



where R_7 = alkylene, substituted alkylene or





where,R_8 is alkylene of 2 to 8 carbons,
R is alkyl of 2 to 25 carbons, and
x = 10 to 100.

8. An elastomeric composition for use in dentistry comprising a compound of the general formula:

$R_1 - (A) - R_2$

wherein R_1 is $CH_2 = \underset{\displaystyle R_3}{\overset{\displaystyle |}{C}} - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O - (R_4) - O - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - \overset{\displaystyle H}{\overset{\displaystyle |}{N}} -$,

R_2 is $CH_2 = \underset{\displaystyle R_3}{\overset{\displaystyle |}{C}} - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O - (R_4) - \overset{\displaystyle H}{\overset{\displaystyle |}{N}} - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O -$,

R_3 is H, alkyl of 2-10 carbons, substituted alkyl of 2-10 carbons, aryl of 6-14 carbons, substituted aryl of 6-14 carbons, F, or CN and R_3 may be the same or different in each position;

R_4 is a divalent hydrocarbon radical or divalent substituted hydrocarbon radical and may be straight or branched chain or cyclic or a combination thereof from 2-10 carbons; and

A is a polyurethane, polyether or polyester group;

a photoinitiator and filler,

wherein substituted represents a chemical substituent selected from the group consisting of halogen, lower alkyl having from 1 to 6 carbon atoms, oxy lower alkyl having from 1 to 6 carbon atoms, silyl lower alkyl having from 1 to 6 carbon atoms, phenyl, halophenyl, alkoxyphenyl,trihalomethyl and dihalomethyl having from 1 to 6 carbon atoms.

9. A composition according to Claim 8 for use as a soft denture liner composition comprising a compound of the general formula:

$R_1 - (A) - R_2$

wherein R_1 is $CH_2 = \underset{\displaystyle R_3}{\overset{\displaystyle |}{C}} - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O - (R_4) - O - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - \overset{\displaystyle H}{\overset{\displaystyle |}{N}} -$,

and R_2 is as defined in Claim 8,

R_3 is H, alkyl of 2-10 carbons, substituted alkyl of 2-10 carbons, aryl of 6-14 carbons, substituted aryl Of 6-14 carbons, F or CN and R_3 may be the same or different in each position

R_4 is a divalent hydrocarbon radical or divalent substituted hydrocarbon radical and may be straight or branched chain or cyclic or a combination thereof having from 2-10 carbons and

A is a polyurethane, polyether or polyester group

a photoinitiator and filler,

wherein substituted represents a chemical substituent selected from the group consisting of halogen, lower alkyl and having 1 to 6 carbon atoms, oxy lower alkyl and having 1 to 6 carbon atoms, silyl lower alkyl and having 1 to 6 carbon atoms, phenyl, halophenyl, alkoxyphenyl, trihalomethyl, and dihalomethyl having from 1 to 6 carbon atoms.

10. The composition of claim 8 or 9 wherein said filler comprises 5 to 95 percent by weight of said composition.

11. The composition of claim 8 or 9 wherein said filler comprises fused quartz or silica.

12. The composition of claim 8 wherein said composition has a molecular weight of 500-4000 and a viscosity suitable for use as an oral bandage or a dental impression material and is non-toxic in use in

the oral cavity, stable in storage for at least one (1) month as a one-component composition when actinic light free, by exposing said composition to light filtered to limited wavelengths substantially within the visible light range to form an oral bandage, a dental impression.

13. The composition of claim 9 wherein said composition has a molecular weight of about 500-4000 and a viscosity suitable for use as a soft denture liner and is non-toxic in use in the oral cavity, stable in storage for at least one (1) month as a one-component composition when actinic light free, by exposing said composition to light filtered to limited wavelengths substantially within the visible light range to form a soft denture liner.

14. The composition of claim 1, 4, 8 or 9 further comprising a medicament.

15. The composition of claim 1, 4, 8 or 9 further comprising an accelerator.

16. The composition of claim 1, 4, 8 or 9 further comprising a titanate accelerator.

17. The composition of claim 8 or 9, wherein said filler has an organosilyl coating.

18. The composition of claim 1, 4, 8, or 9, wherein said filler comprises from 20 to 90 percent by weight of said composition.

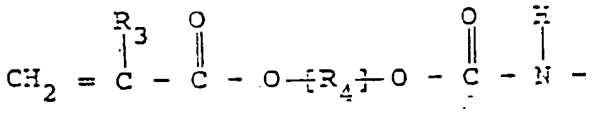
19. The composition of claim 1, 4, 8, or 9, wherein said filler comprises from 40 to 85 percent by weight of said composition.

Patentansprüche

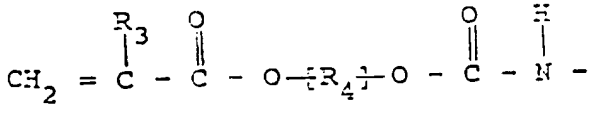
1. Elastomere Zahnabdruckmaterial-Zusammensetzung zur Verwendung im zahnärztlichen Bereich, umfassend eine Verbindung der allgemeinen Formel

$R_1 - (A) - R_2$,

in der R_1



ist, R_2



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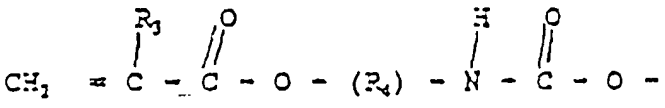


ist,

R_3 H, Alkyl mit 2-10 Kohlenstoffen, substituiertes Alkyl mit 2-10 Kohlenstoffen, Aryl mit 6-14 Kohlenstoffen, substituiertes Aryl mit 6-14 Kohlenstoffen, F oder CN ist und R_3 in jeder Stellung gleich oder verschieden sein kann;

R_4 ein zweiwertiger Kohlenwasserstoffrest oder substituierter zweiwertiger Kohlenwasserstoffrest mit 2-

10 Kohlenstoffen ist und gerad- oder verzweigtkettig oder cyclisch oder eine Kombination davon sein kann; und
A eine Polyurethan-, Polyether- oder Polyestergruppe ist;
5 bis 95 Gew.-% Füllstoffe und einen Photoinitiator, worin substituiert einen chemischen Substituenten bedeutet, der aus der Gruppe ausgewählt ist, die aus Halogen, Niederalkyl mit 1 bis 6 Kohlenstoffatomen, Oxyniederalkyl mit 1 bis 6 Kohlenstoffatomen, Silylniederalkyl mit 1 bis 6 Kohlenstoffatomen, Phenyl, Halogenphenyl, Alkoxyphenyl, Trihalogenmethyl und Dihalogenmethyl mit 1 bis 6 Kohlenstoffatomen besteht, und worin die zusammensetzung ein Molekulargewicht von 500 - 4000 und eine Viskosität aufweist, die zur Verwendung als Mundbandage oder Zahnabdruckmaterial geeignet ist, und bei der Verwendung in der Mundhöhle nicht-toxisch, bei der Lagerung über mindestens einen (1) Monat als Ein-Komponenten-Zusammensetzung unter Ausschluß von aktinischem Licht stabil ist und ein dauerhaftes elastomeres Gedächtnis annimmt, das zur Verwendung als Mundbandage oder Zahnabdruckmaterial geeignet ist, wenn sie eine (1) Minute bis zu einer Tiefe von 2,54 cm (ein (1) Inch) Licht ausgesetzt wird, das so gefiltert ist, daß die Wellenlängen im wesentlichen auf den sichtbaren Lichtbereich beschränkt sind.

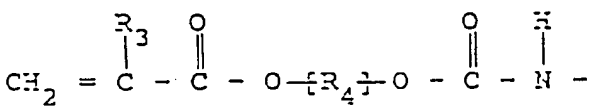
2. Abdruckmaterial für die Anwendung bei Säugergewebe, das in Kontakt mit demselben aushärtet, um den Abdruck desselben festzulegen; wobei das Abdruckmaterial in einer Menge von 5 bis 95 Gew.-% der Gesamtzusammensetzung ein Harz, das durch Initiierung freier Radikale polymerisierbar ist; Alkylbenzolsulfonyltitanat, das in einer Menge von 0,001 bis 2 Gew.-% der Gesamtzusammensetzung vorhanden ist; einen Polymerisationsinitiator, der in einer Menge von 0,001 bis 10 Gew.-% des polymerisierbaren Harzes vorhanden ist; und Füllstoff umfaßt, der in einer Menge von 5 bis 95 Gew.-% der Gesamtzusammensetzung vorhanden ist, in der das poiymerisierbare Harz eine Verbindung der in Anspruch 1 definierten Formel R_1-(A)-R_2 umfaßt.

3. Abdruckmaterial nach Anspruch 2, in dem das Harz, das durch Initiierung freier Radikale polymerisierbar ist, in einer Menge von ungefähr 10 bis 80 Gew.-% der Gesamtzusammensetzung vorhanden ist; das Alkylbenzolsulfonyltitanat Neoalkoxy;(diallyl)oxytri(dodecyl)benzolsulfonyltitanat ist und in einer Menge von 0,005 bis 1 Gew.-% der Gesamtzusammensetzung vorhanden ist; der Polymerisationsinitiator in einer Menge von 0,01 bis 5 Gew.-% des polymerisierbaren Harzes vorhanden ist; und Füllstoff in einer Menge von 20 bis 90 Gew.-% der Gesamtzusammensetzung vorhanden ist.

4. Zusammensetzung nach Anspruch 1 zur Verwendung als weiche Zahnprothesenunterfütterung, umfassend eine Verbindung der allgemeinen Formel:

R_1 - (A) - R_2,

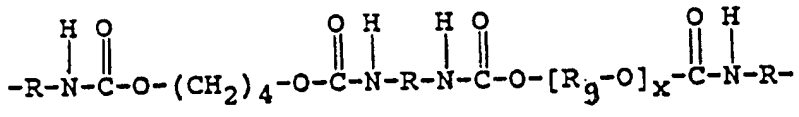
in der R_1



ist und R_2 wie in Anspruch 1 definiert ist,
R_3 H, Alkyl mit 2-10 Kohlenstoffen, substituiertes Alkyl mit 2-10 Kohlenstoffen, Aryl mit 6-14 Kohlenstoffen, substituiertes Aryl mit 6-14 Kohlenstoffen, F oder CN ist und R_3 in jeder Stellung gleich oder verschieden sein kann;
R_4 ein zweiwertiger Kohlenwasserstoffrest oder substituierter zweiwertiger Kohlenwasserstoffrest mit 2-10 Kohlenstoffen ist und gerad- oder verzweigtkettig oder cyclisch oder eine Kombination davon sein kann; und
A eine Polyurethan-, Polyether- oder Polyestergruppe ist;
5 bis 95 Gew.-% Füllstoffe und einen Photoinitiator, worin substituiert einen chemischen Substituenten bedeutet, der aus der Gruppe ausgewählt ist, die aus Halogen, Niederalkyl mit 1 bis 6 Kohlenstoffatomen, Oxyniederalkyl mit 1 bis 6 Kohlenstoffatomen, Silylniederalkyl mit 1 bis 6 Kohlenstoffatomen, Phenyl, Halogenphenyl, Alkoxyphenyl, Trihalogenmethyl und Dihalogenmethyl mit 1 bis 6 Kohlenstoffatomen besteht, und worin die Zusammensetzung ein Molekulargewicht von 500 - 4000 und eine

Viskosität aufweist, die zur Verwendung als weiche Zahnprothesenunterfütterung geeignet ist, und bei der Verwendung in der Mundhöhle nicht-toxisch, bei der Lagerung über mindestens einen (1) Monat als Ein-Komponenten-Zusammensetzung unter Ausschluß von aktinischem Licht stabil ist und ein dauerhaftes elastomeres Gedächtnis annimmt, das zur Verwendung als weiche Zahnprothesenunterfütterung geeignet ist, wenn sie eine (1) Minute bis zu einer Tiefe von 2,54 cm (ein (1) Inch) Licht ausgesetzt wird, das so gefiltert ist, daß die Wellenlängen im wesentlichen auf den sichtbaren Lichtbereich beschränkt sind.

5. Weiche Zahnprothesenunterfütterung nach Anspruch 4, in der (A)



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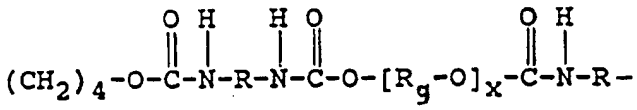


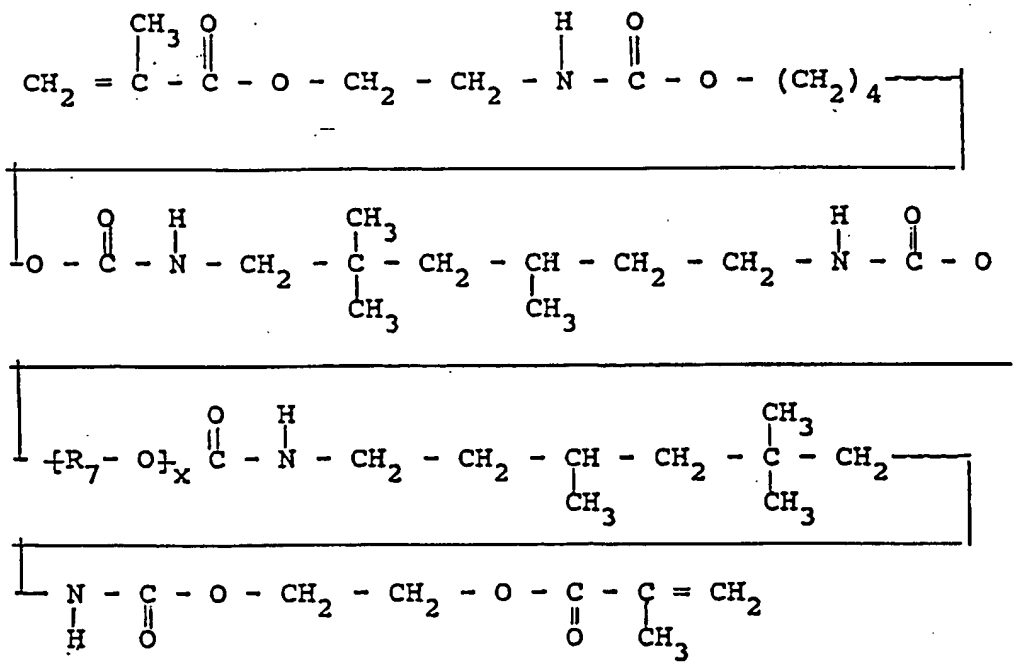
ist, worin R Alkyl mit 2 bis 25 Kohlenstoffen ist, R_9 Alkyl mit 2 bis 25 Kohlenstoffen ist und x 10 bis 100 ist.

6. Weiche Zahnprothesenunterfütterung nach Anspruch 5, worin in der neuen Materialzusammensetzung nach Anspruch 1 in der Verbindung, die durch die besagte allgemeine Formel dargestellt wird, A

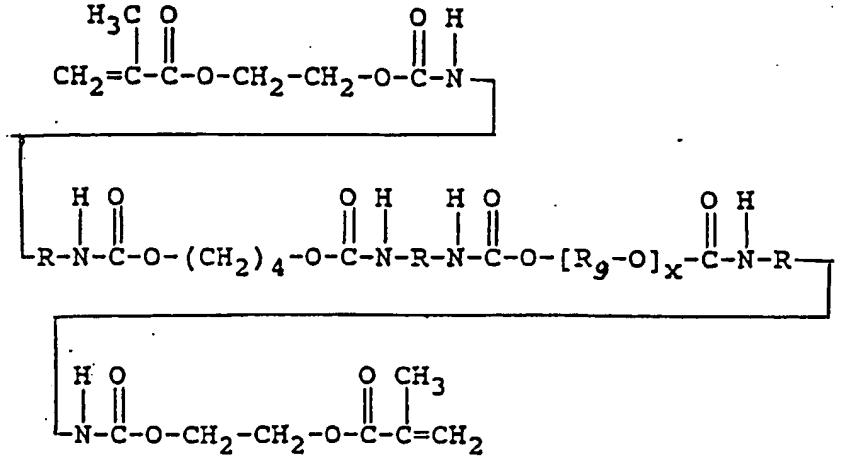
(R_5)-X-(R_6)

ist,
R_5 und R_6 jeweils zweiwertige Kohlenwasserstoffreste oder substituierte zweiwertige Kohlenwasserstoffreste sind, X ein Polyurethan, Polyether oder Polyester ist und R_5-X und R_6-X durch eine Urethanbindung verknüpft sind und R_5 und R_6 2 bis 100 Kohlenstoffatome aufweisen.

7. Weiche Zahnprothesenunterfütterung nach Anspruch 6, umfassend eine Verbindung der allgemeinen Formel



in der R_7 = Alkylen, substituiertes Alkylen, oder

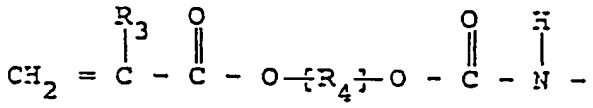


worin R_9 Alkylen mit 2 bis 8 Kohlenstoffen ist, R Alkyl mit 2 bis 25 Kohlenstoffen ist und x = 10 bis 100.

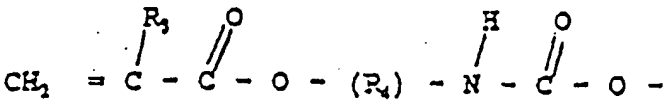
8. Elastomere Zusammensetzung zur Verwendung in der zahnärztlichen Praxis, umfassend eine Verbindung der allgemeinen Formel:

R_1-(A)-R_2,

in der R_1



ist, R_2

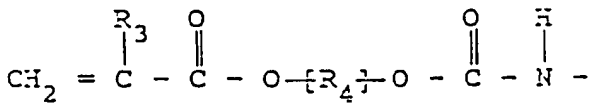


ist,
R_3 H, Alkyl mit 2-10 Kohlenstoffen, substituiertes Alkyl mit 2-10 Kohlenstoffen, Aryl mit 6-14 Kohlenstoffen, substituiertes Aryl mit 6-14 Kohlenstoffen, F oder CN ist und R_3 in jeder Stellung gleich oder verschieden sein kann;
R_4 ein zweiwertiger Kohlenwasserstoffrest oder ein substituierter zweiwertiger Kohlenwasserstoffrest mit 2-10 Kohlenstoffen ist und gerad- oder verzweigtkettig oder cyclisch oder eine Kombination davon sein kann; und
A eine Polyurethan-, Polyether- oder Polyestergruppe ist;
einen Photoinitiator und Füllstoff,
worin substituiert einen chemischen Substituenten bedeutet, der aus der Gruppe ausgewählt ist, die aus Halogen, Niederalkyl mit 1 bis 6 Kohlenstoffatomen, Oxyniederalkyl mit 1 bis 6 Kohlenstoffatomen, Silylniederalkyl mit 1 bis 6 Kohlenstoffatomen, Phenyl, Halogenphenyl, Alkoxyphenyl, Trihalogenmethyl und Dihalogenmethyl mit 1 bis 6 Kohlenstoffatomen besteht.

9. Zusammensetzung nach Anspruch 8 zur Verwendung als weiche Zahnprothesenunterfütterungs-Zusammensetzung, umfassend eine Verbindung der allgemeinen Formel

R_1-(A)-R_2,

in der R_1



ist und R_2 wie in Anspruch 8 definiert ist,
R_3 H, Alkyl mit 2-10 Kohlenstoffen, substituiertes Alkyl mit 2-10 Kohlenstoffen, Aryl mit 6-14 Kohlenstoffen, substituiertes Aryl mit 6-14 Kohlenstoffen, F oder CN ist und R_3 in jeder Stellung gleich oder verschieden sein kann;
R_4 ein zweiwertiger Kohlenwasserstoffrest oder ein substituierter zweiwertiger Kohlenwasserstoffrest mit 2-10 Kohlenstoffen ist und gerad- oder verzweigtkettig oder cyclisch oder eine Kombination davon sein kann; und
A eine Polyurethan-, Polyether- oder Polyestergruppe ist;
einen Photoinitiator und Füllstoff,
worin substituiert einen chemischen Substituenten bedeutet, der aus der Gruppe ausgewählt ist, die aus Halogen, Niederalkyl mit 1 bis 6 Kohlenstoffatomen, Oxyniederalkyl mit 1 bis 6 Kohlenstoffatomen, Silylniederalkyl mit 1 bis 6 Kohlenstoffatomen, Phenyl, Halogenphenyl, Alkoxyphenyl, Trihalogenmethyl und Dihalogenmethyl mit 1 bis 6 Kohlenstoffatomen besteht.

10. Zusammensetzung nach Anspruch 8 oder 9, in der der Füllstoff 5 bis 95 Gew.-% der Zusammensetzung umfaßt.

11. Zusammensetzung nach Anspruch 8 oder 9, in der der Füllstoff Quarzglas oder Siliciumdioxid umfaßt.

12. Zusammensetzung nach Anspruch 8, in der die Zusammensetzung ein Molekulargewicht von 500 - 4000 und eine Viskosität aufweist, die zur Verwendung als Mundbandage oder Zahnabdruckmaterial geeignet ist, und bei der Verwendung in der Mundhöhle nicht-toxisch, bei der Lagerung über mindestens einen (1) Monat als Ein-Komponenten-Zusammensetzungunter Ausschluß von aktinischem Licht stabil ist, um eine Mundbandage, einen Zahnabdruck zu bilden, indem die Zusammensetzung Licht ausgesetzt wird, das so gefiltert ist, daß die Wellenlängen im wesentlichen auf den Bereich des sichtbaren Lichts beschränkt sind.

13. Zusammensetzung nach Anspruch 9, in der die Zusammensetzung ein Molekulargewicht von ungefähr 500-4000 und eine Viskosität aufweist, die zur Verwendung als weiche Zahnprothesenunterfütterung geeignet ist, und bei der Verwendung in der Mundhöhle nicht-toxisch, bei der Lagerung über mindestens einen (1) Monat als Ein-Komponenten-Zusammensetzung unter Ausschluß von aktinischem Licht stabil ist, um eine weiche Zahnprothesenunterfütterung zu bilden, indem die Zusammensetzung Licht ausgesetzt wird, das so gefiltert ist, daß die Wellenlängen im wesentlichen auf den Bereich des sichtbaren Lichts beschränkt sind.

14. Zusammensetzung nach Anspruch 1, 4, 8 oder 9, die weiter ein Medikament umfaßt.

15. Zusammensetzung nach Anspruch 1, 4, 8 oder 9, die weiter einen Beschleuniger umfaßt.

16. Zusammensetzung nach Anspruch 1, 4, 8 oder 9, die weiter einen Titanat-Beschleuniger umfaßt.

17. Zusammensetzung nach Anspruch 8 oder 9, in der der Füllstoff eine Organosilyl-Beschichtung aufweist.

18. Zusammensetzung nach Anspruch 1, 4, 8 oder 9, in der der Füllstoff 20 bis 90 Gew.-% der Zusammensetzung umfaßt.

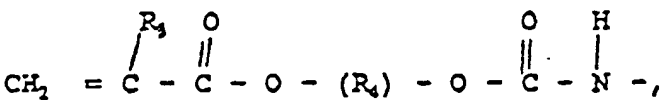
19. Zusammensetzung nach Anspruch 1, 4, 8 oder 9, in der der Füllstoff 40 bis 85 Gew.-% der Zusammensetzung umfaßt.

Revendications

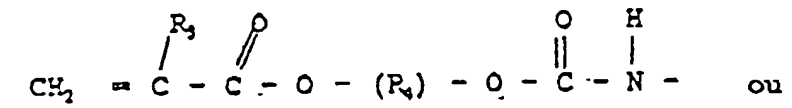
1. Composition d'un matériau d'empreinte dentaire élastomère pour l'utilisation en médecine dentaire comprenant un compose de formule générale

$R_1 - (A) - R_2$

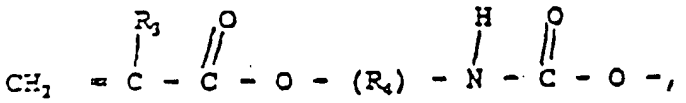
où R_1 est



R_2 est



ou



R_3 est H, un groupe alkyle de 2 à 10 atomes de carbone, un groupe alkyle substitué de 2 à 10 atomes de carbone, un groupe aryle de 6 à 14 atomes de carbone, un groupe aryle substitué de 6 à 14 atomes de carbone, F ou CN et R_3 peut être identique ou différent à chaque position ; R_4 est un radical hydrocarbure bivalent ou un

radical hydrocarbure bivalent substitué et peut être à chaîne linéaire ou à chaîne ramifiée ou cyclique ou une combinaison de ceux-ci, de 2 à 10 atomes de carbone ; et

A est un groupe polyuréthane, polyéther ou polyester ;

de 5 à 95 pour cent en poids de matières de remplissage et un photo-initiateur, où substitué représente un substituant chimique choisi parmi le groupe constitué par l'atome d'halogène, le groupe alkyle inférieur ayant de 1 à 6 atomes de carbone, oxy alkyle inférieur ayant de 1 à 6 atomes de carbone, silyl alkyle inférieur ayant de 1 à 6 atomes de carbone, phényle, halophényle, alcoxyphényl, trihalométhyle et dihalométhyle ayant de 1 à 6 atomes de carbone, et où ladite composition a un poids moléculaire de 500 à 4000 et une viscosité adaptée à l'utilisation comme pansement bucco-dentaire ou matériau d'empreintes dentaires et n'est pas toxique à utiliser dans la cavité buccale, est stable à la conservation pendant au fins un (1) mois comme composition à un composant à l'abri de la lumière actinique et assume une némoire élastomère permanente appropriée pour l'utilisation comme pansement bucco-dentaire ou matériau d'empreintes dentaires lorsque exposé à la lumière filtrée, à des longueurs d'ondes restreintes essentiellement au domaine de la lumière visible pendant une (1) minute à une profondeur de 2,54 cm (un (1) pouce).

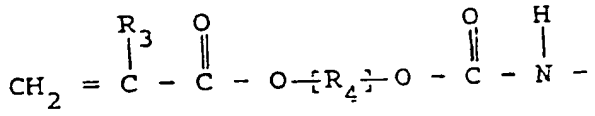
2. Matériau d'empreintes pour l'application au tissu mammifère et le durcissement en contact avec celui-ci pour figer son empreinte ; ledit matériau d'empreintes conprenant une résine polymérisable à radicaux libres initiés présente en quantité de 5 à 95% en poids de la composition totale ; du titanate benzènesulfonyl d'alkyle présent en quantité de 0,001 à 2% en poids de la composition totale ; un initiateur de polymérisation présent en quantité de 0,001 à 10% en poids de la résine polymérisable ; et de la matière de remplissage présente en quantité de 5 à 95% en poids de la composition totale, dans lequel ladite résine polymérisable comporte un composé de formule R_1-(A)-R_2 comme indiqué dans la définition de la Revendication 1.

3. Matériau d'empreintes de la Revendication 2, dans lequel la résine polymérisable à radicaux libres initiés est présente en quantité d'environ 10 à 80% en poids de la composition totale ; ledit titanate benzènesulfonyl d'alkyle est le néoalcoxy ; (diallyl)oxytri(dodécyl)benzènesulfonyl titanate et est présent en quantité de 0,005 à 1% en poids de la composition totale ; ledit initiateur de polymérisation est présent en quantité de 0,01 à 5% en poids de la résine polymérisable ; et la matière de remplissage est présente en quantité de 20 à 90% en poids de la composition totale.

4. Composition selon la Revendication 1, pour l'utilisation comme revêtement mou de prothèse dentaire comprenant un composé de formule générale :

R_1 - (A) - R_2

où R_1 est



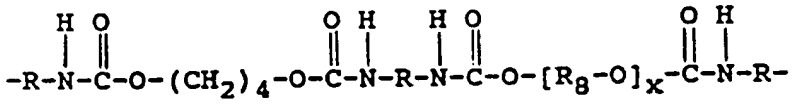
et R_2 est comme indiqué dans la définition de la Revendication 1,

R_3 est H, un groupe alkyle de 2 à 10 atomes de carbone, un groupe alkyle substitué de 2 à 10 atomes de carbone, un groupe aryle de 6 à 14 atomes de carbone, un groupe aryle substitué de 6 à 14 atomes de carbone, F ou CN et R_3 peut être identique ou différent à chaque position

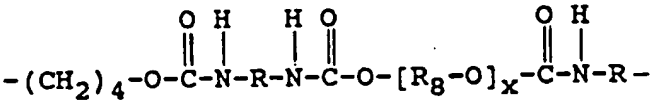
R_4 est un radical hydrocarbure bivalent ou un radical hydrocarbure bivalent substitué et peut être à chaîne linéaire ou à chaîne ramifiée ou cyclique ou une combinaison de ceux-ci, ayant de 2 à 10 atomes de carbone et

A est un groupe polyuréthane, polyéther ou polyester, de 5 à 95 pour cent en poids de matières de remplissage et un photo-initiateur, où substitué représente un substituant chimique choisi parmi le groupe constitué par l'atome d'halogène, le groupe alkyle inférieur ayant de 1 à 6 atones de carbone, oxy alkyle inférieur ayant de 1 à 6 atones de carbone, silyl alkyle inférieur ayant de 1 à 6 atomes de carbone, phényle, halophényle, alcoxyphényl, trihalométhyle et dihalométhyle ayant de 1 à 6 atomes de carbone, et où ladite composition a un poids moléculaire de 500 à 4000 et une viscosité adaptée à l'utilisation comme revêtement mou de prothèse dentaire et n'est pas toxique à utiliser dans la cavité buccale, est stable à la conservation pendant au fins un (1) mois comme composition à un composant à l'abri de la lumière actinique et assume une mémoire élastomère permanente appropriée pour l'utilisation comme revêtement mou de prothèse dentaire lorsque exposé à la lumière filtrée, à des longueurs d'ondes restreintes essentiellement au domaine de la lumière visible pendant une (1) minute à une profondeur de 2,54 cm (un (1) pouce).

5. Revêtement mou de prothèse dentaire de la revendication 4, dans lequel (A) est



ou



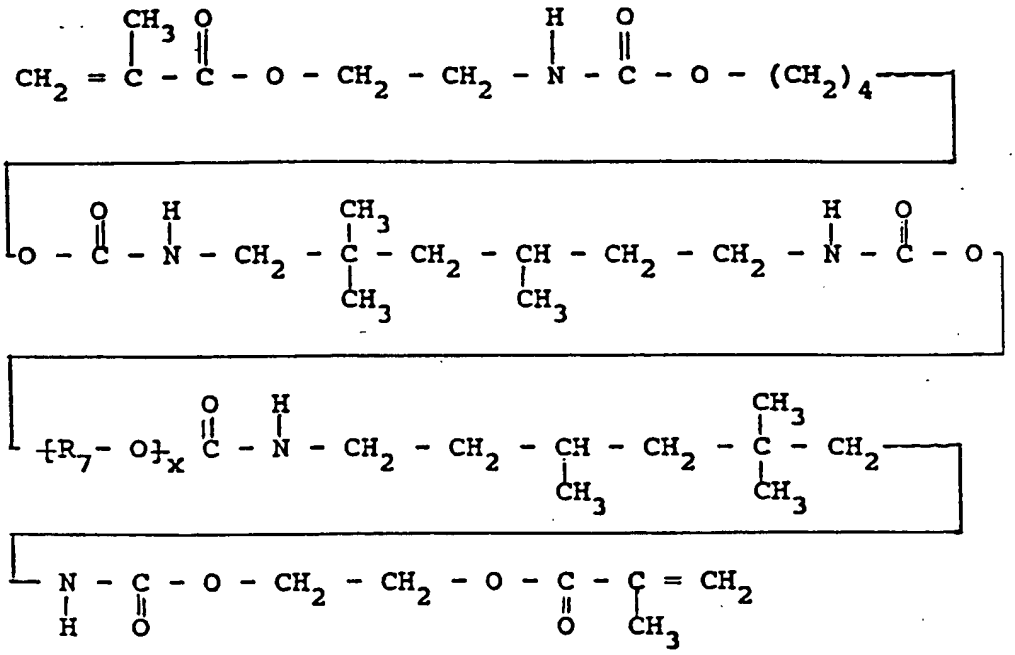
où R est un groupe alkyle de 2 à 25 atomes de carbone, R_8 est un groupe alkyle de 2 à 25 atomes de carbone et x vaut 10 à 100.

6. Revêtement mou de prothèse dentaire de la revendication 5, dans lequel la nouvelle composition de matière de la Revendication 1 contenant lesdits composés, fournit cette formule générale

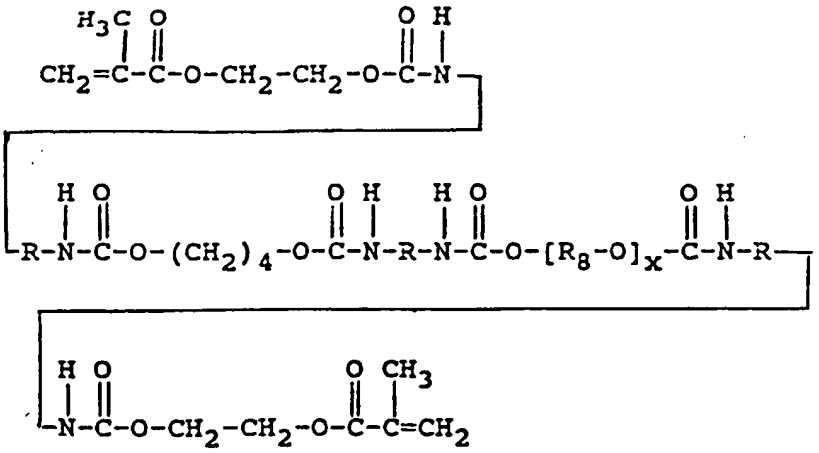
A est (R_5) - X -(R_6)

R_5 et R_6 sont chacun des radicaux hydrocarbures bivalents ou des radicaux hydrocarbures bivalents substitués, X est un polyuréthane, un polyéther ou un polyester et R_5-X et R_6-X sont réunis par une liaison uréthane et R_5 et R_6 ont de 2 à 100 atomes de carbone.

7. Revêtement mou de prothèse dentaire de la Revendication 6, comprenant un composé de formule générale



où R7 = un groupe alkylène, un groupe alkylène substitué ou

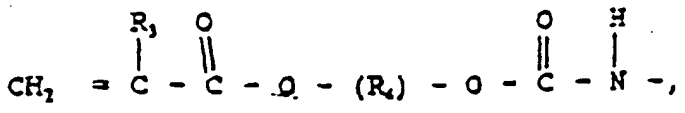


où R_8 est un groupe alkylène de 2 à 8 atomes de carbone,
R est un groupe alkyle de 2 à 25 atomes de carbone, et
x = 10 à 100.

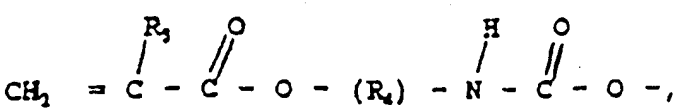
8. Composition élastomère pour l'utilisation en médecine dentaire comprenant un composé de formule générale :

R_1 - (A) - R_2

où R_1 est



R^2 est



R_3 est H, un groupe alkyle de 2 à 10 atomes de carbone, un groupe alkyle substitué de 2 à 10 atomes de carbone, un groupe aryle de 6 à 14 atomes de carbone, un groupe aryle substitué de 6 à 14 atomes de carbone, F ou CN et R_3 peut être identique ou différent à chaque position ;

R_4 est un radical hydrocarbure bivalent ou un radical hydrocarbure bivalent substitué et peut être à chaîne linéaire ou à chaîne ramifiée ou cyclique ou une combinaison de ceux-ci, de 2 à 10 atomes de carbone ; et

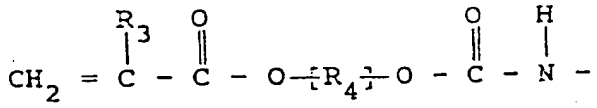
A est un groupe polyuréthane, polyéther ou polyester ;

un photo-initiateur et une matière de remplissage, où substitué représente un substituant chimique choisi parmi le groupe constitué par l'atome d'halogène, le groupe alkyle inférieur ayant de 1 à 6 atomes de carbone, oxy alkyle inférieur ayant de 1 à 6 atomes de carbone, silyl alkyle inférieur ayant de 1 à 6 atomes de carbone, phényle, halophényle, alcoxyphényl, trihalométhyle et dihalométhyle ayant de 1 à 6 atomes de carbone.

9. Composition selon la Revendication 8 pour l'utilisation comme composition de revêtement mou de prothèse dentaire conprenant un composé de formule générale :

R_1 - (A) - R_2

où R_1 est



et R2 est comme indiqué dans la définition de la Revendication 8,

R_3 est H, un groupe alkyle de 2 à 10 atomes de carbone, un groupe alkyle substitué de 2 à 10 atomes de carbone, un groupe aryle de 6 à 14 atomes de carbone, un groupe aryle substitué de 6 à 14 atomes de carbone, F ou CN et R_3 peut être identique ou différent à chaque position ;

R_4 est un radical hydrocarbure bivalent ou un radical hydrocarbure bivalent substitué et peut être à chaîne linéaire ou à chaîne ramifiée ou cyclique ou une combinaison de ceux-ci, ayant de 2 à 10 atomes de carbone et

A est un groupe polyuréthane, polyéther ou polyester

un photo-initiateur et une matière de remplissage, où substitué représente un substituant chimique choisi parmi le groupe constitué par l'atome d'halogène, le groupe alkyle inférieur et ayant 1 à 6 atomes de carbone, oxy alkyle inférieur et ayant 1 à 6 atomes de carbone, silyl alkyle inférieur et ayant 1 à 6 atomes de carbone, phényle, halophényle, alcoxyphényl, trihalométhyle et dihalométhyle ayant de 1 à 6 atomes de carbone.

10. Composition de la revendication 8 ou 9, dans laquelle ladite matière de remplissage comporte 5 à 95 pour cent en poids de ladite composition.

11. Composition de la revendication 8 ou 9, dans laquelle ladite matière de remplissage comporte du quartz ou de la silice fondus.

12. Composition de la revendication 8, dans laquelle ladite composition a un poids moléculaire de 500 à 4000 et une viscosité adaptée à l'utilisation comme pansement bucco-dentaire ou matériau d'empreintes dentaires et n'est pas toxique à utiliser dans la cavité buccale, est stable à la conservation pendant au moins un (1) mois comme composition à un composant à l'abri de la lumière actinique, par exposition de ladite composition à la lumière filtrée, à des longueurs d'ondes restreintes essentiellement au domaine de la lumière visible pour former un pansement bucco-dentaire, une empreinte dentaire.

13. Composition de la revendication 9, dans laquelle celle-ci a un poids moléculaire d'environ 500 à 4000 et une viscosité adaptée à l'utilisation comme revêtement mou de prothèse dentaire et n'est pas toxique à utiliser dans la cavité buccale, est stable à la conservation pendant au moins un (1) mois comme composition à un composant à l'abri de la lumière actinique, par exposition de ladite composition à la lumière filtrée, à des longueurs d'ondes restreintes essentiellement au donaine de la lumière visible pour former un revêtement mou de prothèse dentaire.

14. Composition de la revendication 1, 4, 8 ou 9 comportant en outre un médicament.

15. Composition de la revendication 1, 4, 8 ou 9 comportant en outre un accélérateur.

16. Composition de la revendication 1, 4, 8 ou 9 comportant en outre un accélérateur à titanate.

17. Composition de la revendication 8 ou 9, dans laquelle ladite matière de remplissage a un revêtement d'organosilyle.

18. Composition de la revendication 1, 4, 8 ou 9, dans laquelle ladite matière de remplissage comporte de 20 à 90 pour cent en poids de ladite composition.

19. Composition de la revendication 1, 4, 8 ou 9 dans laquelle ladite matière de remplissage comporte de 40 à 85 pour cent en poids de ladite composition.